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THE LAWS GOVERNING THE RATE AT WHICH METALS ARE DISSOLVED IN CONCENTRATED ACIDS. I

Ya. V. Durdin

When metals are dissolved in concentrated acids, we get two types of curves representing the variation of the rate of dissolution of the metal with the acid concentration: curves without any maximum and curves having a maximum.

Curves without any maximum have been obtained by Conroy [1], by Oranskaya and the present author [2,3], and by Krasilshchikov [4] for the dissolution of iron in hydrochloric and sulfuric acids at concentrations up to 10 N; Tsentnershver secured such curves for the dissolution of cadmium [5], tin [6], and aluminum [7] in hydrochloric acid. Similar curves have been plotted for cadmium and aluminum in our laboratory as well. On the other hand, Kayander [8] long ago pointed out that when magnesium was dissolved in concentrated acids the function V(c) is represented by curves exhibiting a maximum. V(c) curves with a maximum were secured by E. Müller [9], as well as by the present author and A.M.Markevich [10] for the dissolution of chromium in hydrochloric acid, though we showed that this maximum vanished when the solution was stirred sufficiently during dissolution. In the same papers it was shown that the V(c) curves exhibited a maximum for the dissolution of chromium in sulfuric acid as well (without stirring), this maximum being located at about 12 N H_2SO_4 in our tests. Ram [11] and Damon [12] secured a maximum on the V(c) curves for the dissolution of iron in sulfuric acid of about 13-14 N (again in tests carried out without stirring the solution).

Several authors – Tsentnershver [13], Kayander [8], and Müller [9] – have commented that the V(c) curves with maxima for the dissolution of metals resemble the specific conductance – acid concentration curves, Palmayer considering this to be a direct proof that the equation of the theory of local elements was correct. Tsentnershver, on the other hand, found that the variation of the rate of metal dissolution with the acid concentration could be expressed by the general equation:

$$V = kc^n, \qquad (1)$$

where $n > 1$, for the dissolution of cadmium, tin, and aluminum he had investigated and came to the conclusion that in these instances we must reject the concept of the electrochemical mechanism of the dissolution of metals, proposing instead another mechanism, which he called "chemical" [14]. We believe that both views, that of Palmayer as well as that of Tsentnershver, are wrong, though we must admit that, independent of their views, the notion that the V(c) curves with and without a maximum represent different mechanisms of interaction between metal and acid is fairly plausible at first glance. We shall, therefore, begin by endeavoring to furnish an explanation for the existence of a maximum on the V(c) curves, at the same time demonstrating that both types of curves can exist for one and the same mechanism of metal-acid interaction.

The Mechanism Governing the Appearance of a Maximum on the Curves Representing the Variation of the Rate of Dissolution of Metals with Acid Concentration

Tsentnershver [13] long ago noted that the position of the maximum on the V(c) curve and on the $\varkappa$(c) curve did not coincide altogether for the dissolution of magnesium in acetic acid. According to Kayander, the maximum on the V(c)-curve is located at approximately 6.5 N acetic acid, while the maximum conductance of acetic acid is located at about 2.5 N.

The discrepancy between the positions of the maximum on the V(c) and $\varkappa$(c) is even greater in the dissolution of iron in sulfuric acid, Damon [12] finding that the maximum of the V(c) curve occurs at about a 13-14 N acid, while the maximum conductance of sulfuric acid lies at a concentration of about 8 N. These facts are evidence against the theory that the maximum of the conductance curve is the underlying reason for the maximum on the curve for the rate of metal dissolution. The most convincing confirmation of this conclusion, in our opinion, is our observation that the maximum on the curve showing the variation of the dissolution of chromium with the concentration of hydrochloric acid vanishes when the solution is stirred vigorously enough. For convenience's sake, this curve is reproduced in Fig. 1. The curve abc in this figure was plotted for an unstirred solution ($\omega = 0$), the curves ab'c' and ab"c" representing $\omega = 130$ and 200 stirrer rpm, respectively. The curve abb"', without a maximum, was plotted at $\omega = 370$ rpm.

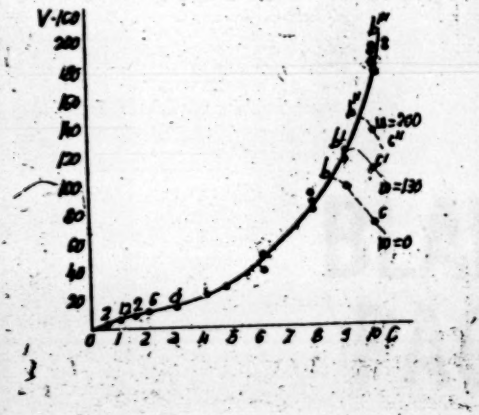

Fig. 1

We see from Fig. 1 that the position of the maximum on the V(c) curve shifts as the rate of stirring rises. At $\omega = 370$ rpm the maximum vanishes altogether, the variation of the rate at which the chromium dissolves with the concentration of the hydrochloric acid being given by an exponential curve resembling the curves plotted for the dissolution of iron, cadmium, tin, and zinc.

We may conclude from what has been set forth above that the mechanism governing metal dissolution is apparently the same in the curves with a maximum and without one, the fundamental type being the curve without any maximum. The appearance of a maximum on these curves is due to some auxiliary controlling factor, which is not always manifested and is not the result of a decrease in the specific conductance of the acid. We believe that the appearance of this maximum is caused by the passivation of the metal surface that occurs at high acid concentrations, though this passivation may be due to different factors in different instances. Let us begin by considering the maximum on the V(c) curve for the dissolution of chromium in hydrochloric acid, since we know the change in the shape of this curve that occurs when the solution is stirred. In our discussion it is convenient to have an expression for the rate of reaction at the surface of the metal as a function of the acid concentration and an expression for the rate at which the reaction products are carried away from the surface of the metal into the solution. We do not need precise expressions for these rates, however, all we require being

equations that correctly express the general nature of the behavior patterns involved. Nor are we now interested in the mechanism of the reactions taking place at the surface of the metal.

Accordingly, we represent the variation of the reaction rate at the surface of the metal with the concentration of the acid by Equation (1):

$$V_n = kc^n,$$

which agrees with the experimental data for the variation of the rate of metal dissolution with acid concentration in the region up to the maximum, provided the diffusion process does not affect it perceptibly.

We shall use the equation:

$$V_D = k(\omega^m + a) \cdot c_n \qquad (2)$$

for the rate at which the dissolved metal is carried away into the solution from the surface of the metal,* where c_n is the concentration of the metal salt at the metal surface (for the sake of simplicity, we assume that the concentration of the metal salt in the solution is zero); ω is the stirrer rpm; and m is an exponent whose values lie between 0.5 and 1. The variable (a) represents the intensity of the stirring due to the movement of hydrogen bubbles at the surface of the metal. In both of these equations the rates V_n and V_D are based on a unit of the geometrical surface of the metal.

Let us now consider the rate at which chromium dissolves as a function of the concentration of the hydrochloric acid. According to the data set forth in our paper written together with A.N.Markevich, the rate at which chromium dissolves in hydrochloric acid whose concentration is lower that that at the point (b) on the curve of Fig. 1 is independent of the effectiveness with which the solution is stirred. Hence, in the case of the dissolution of chromium, we may set the effect of diffusion processes as practically equal to zero in this range of hydrochloric acid concentrations,** so that Equation (1) is a valid expression of the rate at which chromium dissolves. Figure 2 is a schematic representation of the V(c) curve, corresponding to this equation (the curve abb"). Furthermore, in the stationary state V_D must equal V_n, i.e.:

$$k(\omega^m + a)c_n = kc^n.$$

In the range of acid concentrations under discussion this equation may be readily imagined to occur in consequence of the fact that the concentration of the salt at the metal surface, (c_n), automatically becomes such as to make

$$V_D = V_n.$$

Thus, the leveling out of the rates is due here to the adjustment of the rate of the diffusion process to the reaction

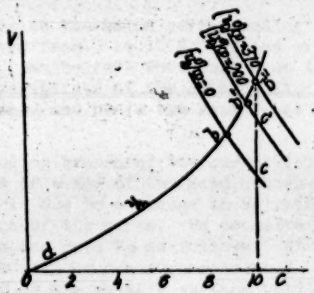

Fig. 2.

*We shall not go into the question of how the metal is diffused in the solution - as free cations, or, say, as more complicated complex ions. We believe that in every instance this rate is an increasing function of the metal salt at the metal surface; for the sake of simplicity we assume that it is proportional to that concentration.

**This applies to the diffusion of the salt from the surface of the metal into the solution as well as to the diffusion of the reagent to the metal surface.

rate at the metal surface, which conforms with the assumption that in this case it is this reaction that governs the kinetics of the metal's dissolution.*

Such a mechanism of adjusting the rates of these processes of ours is confined, however, to a limit that is represented by the condition that $c_n = C_n^*$, where C_n^* is the concentration of the metal salt in a saturated solution of the same. Likewise, the rate V_D corresponding to the given value of ω and of the acid concentration can also rise only to a certain limiting value V_D^*, equal to $k'c_n^*$, where

$$k' = k(\omega^m + a). \qquad (3)$$

It should likewise be borne in mind that the value of C_n^* must drop rapidly as the acid concentration rises, and that, hence, the value of the rate V_D^* must also drop in accordance with Equation (3). The descending curves in Fig. 2 are a schematic representation of the rate V_D^* as a function of the acid concentration, each of the curves corresponding to a given value of ω, as noted on the curve. Let us consider the dissolution of chromium at $\omega = 0$. Since, according to Fig. 2, the curve $[V_D^*]_{\omega=0}$ lies above the V_n curve at concentrations up to 8 N, $V_n = V_D < V_D^*$ in this concentration range, and hence, $c_n < C_n^*$. Accordingly, the factor governing the kinetics of metal dissolution here will be the reaction taking place at the metal's surface, and the rate of metal dissolution will rise, in accordance with the shape of the V_n curve (the a – b section). But this increase in the rate will be paralleled by an increase in the value of c_n, while the variable C_n^* will decrease (owing to the rise in the concentration of the acid). At the point b the rate V_D equals the rate V_D^*, while c_n equals C_n^*. Now any further increase in the rate of the diffusion process as the result of an increase in c_n becomes impossible. Moreover, as the acid concentration rises still further the value of C_n^* will have to start dropping off, as a result of which the rate V_D^* will also begin to fall (in accordance with the curve for $\omega = 0$, along the stretch from b to c). As the acid concentration is raised to 10 N, this rate must fall to the value corresponding to the point c, but since the condition $V_n = V_D$ for the stationary regime must be fulfilled, the rate V_n must also fall to the value corresponding to the point c. Therefore, the rate of dissolution of the metal actually passes through a maximum at the point b.

We still have to explain why the rate V_n drops to the value corresponding to the point c when the acid concentration is raised from 8 to 10 N, instead of rising to the value corresponding to the point b". We believe that this drop is due to the deposition on the metal surface of a precipitate of the metal salt, so that the active surface of the metal is diminished and hence the rate V_n as well.

In other words, we believe that on the descending branch of the curve V(c), where the value of V_D^* is fixed by the given values of ω and of the acid concentration, the levelling out of the rates V_n and V_D is due to a change in V_n rather than in V_D, as was the case on the ascending branch of the curve. We conceive the mechanism of this adaptation of the rate V_n to the rate V_D as follows. At $V_n > V_D$, the solution at the surface of the metal will become supersaturated with the latter's salt, which will be precipitated on the metal's surface until the diminution of the reactive metal surface causes the rate V_n to equal the rate V_D. At $V_n < V_D^*$, the reverse process takes place; the deposit of salt on the metal's surface will dissolve, so that the active surface will increase until the rate V_n equals the rate V_D^*.

It is readily seen from the family of curves reproduced in Fig. 2 that as the stirring rate is increased, the position of the maximum on the V(c) curve must shift toward higher acid concentrations, which agrees with the data of Fig. 1. In general, if we imagine that the portions of the descending V_D^* curves in Fig. 2

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*The rate at which the reagent diffuses toward the surface of the metal will adapt itself to the rate V_n as a result of the corresponding minute changes in the concentration of the reagent at the metal surface.

that lie above the V(c) curve are discarded, we get a family of curves that are quite like the family of experimental curves reproduced in Fig. 1.

The mechanism involved in the formation of a maximum on the V(c) curve proposed by us also provides a good explanation of the peculiarities we have observed in the effect of stirring upon the rate of solution of chromium in hydrochloric acid. These peculiarities are as follows: up to a certain acid concentration, about 8 N, the rate at which the chromium dissolves is independent of any stirring of the solution, while at higher acid concentrations a pronounced stirring effect is manifested; this effect, however, is characterized by the existence of a limiting stirring rate, above which the rate of solution again becomes independent of the rate of stirring. For the sake of convenience, we reproduce in Fig. 3 the curve plotted by A.M.Markevich and the present author [10] that illustrates the variation of the rate at which chromium is dissolved in 10 N hydrochloric acid with the stirrer rpm ω. This phenomenon may be readily explained as follows with the aid of Fig. 2. Let us assume that we are observing the dissolution of chromium in 10 N hydrochloric acid at ω = 0; then the rate of solution of chromium must be that given by point C in Fig. 2. As the stirring rate is raised to ω = 200 rpm, the rate of solution of the chromium rises to the value given by the point c', the rate of the diffusion process rising as the direct result of the increase in the stirring rate, while the reaction rate at the surface of the metal rises as the result of the dissolution of part of the salt deposited on the metal surface and the corresponding increase in the active area of the surface. When the ω is increased to 370 rpm, the rate of solution rises to the value given by the point b', the metal surface being completely freed of the precipitate. Any further increase in ω can then have no effect on the rate at which the chromium dissolves, since it leads merely to the condition $c_n < C_n^*$, at which the factor controlling the kinetics of the process is the reaction at the metal's surface, the rate of which does not depend upon ω when there is no deposit of salt upon the surface. It is obvious that the variation of V with ω will then be expressed by the curve shown in Fig. 3. Thus, the mechanism we have suggested provides a satisfactory explanation of the fairly complicated system of behavior patterns involved in the manifestation of a maximum on the V(c) curve for the dissolution of chromium in hydrochloric acid. We might also mention that this explanation of the maximum is also of fundamental significance, since it illustrates the possibility of abrupt changes in the relationship between the effects of two consecutive processes. Actually, in the case in question the factor controlling the kinetics of dissolution of the metal to the left of the maximum was the reaction at the metal's surface, whereas to the right of the maximum the appearance of a new phase in the system (the salt deposit) made the process of the diffusion of the reaction products the factor that governed the kinetics of the metal's dissolution. The controlling factor likewise changes – the area of the active surface begins to act as this factor instead of the concentration c_n.

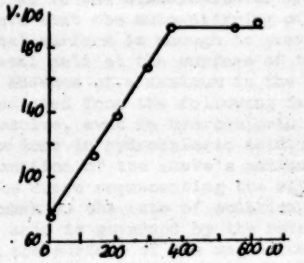

Fig. 3.

It may be thought that the explanation of the maximum on the V(c) curve we have suggested for the dissolution of chromium also applies to the dissolution

other metals in other acids. In support of this we have the following considerations. According to this explanation, curves exhibiting a maximum will be secured whenever the concentration of the metal salt at the metal surface reaches saturation; the higher the rate of dissolution of the metal, the weaker the stirring of the solution, the lower the solubility of the metal salt, and the higher the acid concentration, the faster will saturation set in. These assertions are buttressed by the following facts. We got a maximum on the V(c) curve for the dissolution of chromium in hydrochloric acid at 8-9 N hydrochloric acid (at ω = 0), and at 12 N sulfuric acid for dissolution in that acid, which may be explained as due to the fact that chromium dissolves in sulfuric acid at a much lower rate than in hydrochloric acid. In Damon's experiments mentioned above, the maximum on the V(c) curve was also shifted toward somewhat lower concentrations of sulfuric acid for the grades of steel that dissolved most rapidly. Whenever curves without any maximum are secured for the dissolution of a metal, even when there is no stirring of the solution, as in the dissolution of iron, cadmium, or zinc in hydrochloric acid, we believe that the auto-stirring of the solution due to the hydrogen evolved at the metal surface is encugh to prevent the formation of a saturated solution of the metal salt at the surface of the dissolving metal. Regarded in this light, the absence of a maximum in the dissolution of cadmium and tin could have been predicted from the following facts: 1) the comparatively low rate at which they dissolve, even in hydrochloric acid; 2) the tendency of these metals to form complex ions in hydrochloric acid. It might be thought at first glance that our explanation of the curve's maximum does not hold for the case of the maximum on the curve representing the rate at which magnesium dissolves in acetic acid, inasmuch as the rate of solution of magnesium in moderate concentrations of acetic acid is governed by the rate at which the molecules of the acid diffuse toward the surface of the magnesium rather than by the rate of the chemical reaction at the latter's surface. This is not the case, however; in this instance, the variation of the rate of diffusion of the acid molecules toward the surface of the magnesium (and, hence, the variation of the rate of solution of the magnesium) with the concentration of this acid may be expressed by Equation (1), with $n = 1$. Thus, all our arguments apply here as well, the sole difference being that when magnesium is dissolved in acetic acid, the appearance of a maximum will be governed by the abrupt change in the relative weight of the two diffusion processes, since the factor controlling the kinetics of magnesium dissolution will be the diffusion of the acid toward its surface on the ascending branch of the V(c) curve, and the diffusion of the magnesium salt into the solution on the descending branch.

Nor does the high temperature coefficient we measured for the rate at which chromium is dissolved in 10 N HCl at ω = 0 disprove this explanation, since the increase in the rate at which the chromium salt is diffused from the chromium's surface into the solution must be governed not only by the increase in the diffusion coefficient, but also by the increase in the solubility of the salt (i.e., the increase in C_n^s), the temperature coefficient of which may be high.

Lastly, we must also point out that Evans put forward the concept of a protective film of ferric sulfate as the reason for the passivation of iron in sulfuric acid. In Damon's paper [12] this hypothesis was confirmed by the following: iron plates passivated in sulfuric acid were first quickly washed with cold water and then placed in a beaker with warm water, where the whitish film on the surface of the plates disappeared within a few minutes, after which the plates became active again, ions of iron and of $SO_4^{"}$ being detected in the water.

It may therefore be concluded that the explanation we have advanced for the mechanism and the laws governing the appearance of a maximum on the V(c) curve observed during the dissolution of metals is applicable fairly generally.

Moreover, it must be borne in mind that the phenomenon of passivation in the dissolution of such metals as chromium, and probably iron as well, in concentrated sulfuric acid, especially at high temperatures, may be due to the oxidizing effect of the sulfuric acid as well as to the deposition of the metal's salt upon its surface.

SUMMARY

1. The problem of the cause that produces a maximum on the V(c) curves representing the variation of dissolution of metals with acid concentration has been examined.

2. It has been shown that this maximum is not related to the maximum conductance of the acid.

3. The occurrence of a maximum on the V(c) curve representing the dissolution of chromium in hydrochloric acid has been used to demonstrate that this maximum may be explained by assuming that the rate at which the chromium dissolves is governed by the rate of the reaction occurring at the surface of the metal at the acid concentrations lying along the ascending branch of the V(c) curve, while it is governed by the diffusion of the metal's salt or its ions from the surface of the metal into the solution of the acid at the latter's concentrations on the descending branch of the same curve, the concentration of the metal's salt at the latter's surface attaining concentration at the point where the maximum occurs on the V(c) curve.

LITERATURE CITED

[1] J.Conroy, J.Soc.Chem.Ind., 20, 316 (1901).

[2] M.Cranskaya, Sci. Notes. Leningrad State University, Chem. Series, 3, 54, 235 (1940).

[3] Ya.Durdin and M.Oranskaya, J.Gen.Chem. 21, No. 4, (1951).

[4] A.Krasilshchikov, J.Gen.Chem. 14, 261 (1944).

[5] M.Tsentnershver, Z. phys. Chem., 137, 352 (1928).

[6] M.Tsentnershver, Z. phys. Chem., 141, 167 (1929).

[7] M.Tsentnershver, Z. phys.Chem. 122, 455 (1926).

[8] N.Kayander, J.Russ.Phys.Chem.Soc., 13, 457 (1881); 12, 61 (1880).

[9] E. Müller, Z. phys. Chem., 159, 68 (1932).

[10] Ya.Durdin and A.Markevich, J.Gen.Chem. 19, 2131 (1949). •

[11] S.Ram, J.Soc. Chem. Ind., 54, 107 (1935).

[12] G.Damon, Ind.Eng.Chem. 33, 67 (1941).

[13] M.Tsentnershver, J.Russ.Phys.Chem.Soc., 47, 1064 (1915).

[14] M.Tsentnershver, Trans. Mendeleev Jubilee Congress II, 254 (1937).

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• See CB translation p. a-605 ff.

THE DETECTION AND DETERMINATION OF MINUTE QUANTITIES OF ZIRCONIUM IN PLATINUM

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Zirconium may occur as an unwanted impurity in platinum and platinum alloys when they are melted in zirconium crucibles. Controlling the traces of zirconium in molten platinum is of considerable importance for correct technological processing. We have not come across any data in the literature on the separation of zirconium from platinum or the determination of zirconium in platinum. Colorimetry without the use of shavings seemed best suited for the detection of minute amounts of zirconium in platinum, of the order of hundredths or thousandths of one per cent. We tested various dyes for their fractional detection of zirconium with a view toward their employment in colorimetric determination. We know that the tetravalent zirconium ion forms colored inner coordination compounds with polyhydroxyanthraquinones. Herman Liebhafsky and Winslow [1], for example, comment on their suitability for the colorimetric determination of zirconium. T.A. Uspenskaya, E.I.Guldina, and M.S.Zverkova [2] employed the colorimetric titration of a zirconium-alizarin coordination compound [3] for the rapid determination of zirconium in ferrozirconium.

Our qualitative and approximately quantitative tests of polyhydroxyanthraquinones (alizarin-1,2-dihydroxyanthraquinone; quinizarin-1,4-dihydroxyanthraquinone; quinalizarin-1,2,5,8-tetrahydroxyanthraquinone; alizarin S; etc.) showed that quinalizarin was the most sensitive, but its very low solubility in water, its critical shortage, and its formation of a colored compound with Pt^{++++} made us choose sodium alizarinsulfonate, which constitutes stable aqueous solutions that can be used for qualitative as well as quantitative zirconium determinations. In pure salts the tetravalent zirconium ion can be detected in concentrations of 10^{-5} and $2 \cdot 10^{-6}$ g per ml by means of sodium alizarinsulfonate, which forms a rose-colored coordination compound. The solution pH has a pronounced effect upon the intensity of the color, especially at low concentrations of the zirconium ion. At 10^{-5} g of zirconium per ml, for instance, the alizarin zirconium lake is broken down completely at a pH of 1, the color being preserved at a pH of about 2.

At concentrations approaching 10^{-6} g zirconium per ml, the intensity of the rose color is so slight that the yellow of alizarin S overshadows the pink of the alizarin zirconium lake. When the solution is agitated with chloroform (or gasoline, amyl acetate, or carbon tetrachloride), flotation of the lake takes place after a few seconds of standing, and a rose-colored film makes its appearance at the interphase boundary. Thus, the flotation of an alizarin zirconium coordination compound with chloroform or gasoline increases the sensitivity of the reaction for detecting zirconium with alizarin S to 10^{-6} g of zirconium per ml.

Detection procedure. 1-2 drops of concentrated hydrochloric acid and 1 drop of a 0.2% aqueous solution of sodium alizarinsulfonate are added to 2-3 ml

a solution of zirconium nitrate, the whole is agitated, about 0.5 ml of chloroform is added, and the mixture is shaken up again and allowed to stand. The tiny drops of chloroform produced by the shaking become covered with a rose-colored film of an alizarin zirconium coordination compound at the bottom of the test tube. When the mixture has stood for a longer time, the color becomes concentrated at the interphase boundary.

The detection of traces of zirconium in platinum of the order of hundredths or thousandths of one per cent requires a preliminary separation of the platinum from the zirconium. We found it best to separate such minute quantities of zirconium in the solid phase, using the series rule. Eliminating impurities from the solution by the series rule involves the action of another precipitate that has a high K_s upon the solution [4]. Inasmuch as tetravalent zirconium is precipitated by the carbonate ion, and the carbonates of magnesium and of the alkali-earth metals have the highest K_s values in the carbonate series, the action of these latter carbonates upon a solution containing a zirconium ion ought to precipitate the latter. Tests have shown that when a solution of zirconium nitrate is agitated with a suspension of $CaCO_3$ ($MgCO_3$, $SrCO_3$, $BaCO_3$), then heated to boiling, and set aside to stand, and the precipitate filtered out, the precipitate left on the filter contains zirconium and the excess carbonate. The precipitate is dissolved in concentrated hydrochloric acid, sodium hydroxide is added until the solution turns cloudy, the cloudiness is dissolved by adding a few drops of the hydrochloric acid, and then a little more acid is added until the pH is about 2. The pH is determined with buffer solutions by means of a drop test on paper, applying a drop of the solution under test to a ash-free filter and then adding a drop of methyl violet. At a pH of approximately 2 we get a lilac-colored spot with a blue rim. At this acidity magnesium and calcium ions do not form colored complex inner salts with alizarin S, whereas the solution turns rose-colored when zirconium is present. At concentrations that are less than 10^{-5} g of zirconium per ml it is better to detect the zirconium by flotation of the alizarin zirconium lake with chloroform.

We determined zirconium quantitatively by colorimetric analysis of the alizarin zirconium coordination compound. In this test, however, colorimetric analysis is hampered by the fact that alizarin S has a color of its own, but if we use only a limited amount of the reagent (alizarin S) and keep its concentration constant, the colorimetric determination may be made with sufficient accuracy without resorting to special optical methods of measurement.

We employed the procedure and technique used in N.A.Tananaev's shavingless method [5]. The colorimetry technique involves the balancing of the colors of a standard and a test solution in identical 10-ml measuring cyliders. To keep the concentration of the alizarin S and the acidity of the solution constant, colorimetric analysis is done by diluting a liquid containing one drop of a 0.04% aqueous solution of alizarin S and two drops of hydrochloric acid (3:1). This dye concentration and acidity (pH ~ 2) ensure the appearance of the color of the alizarin zirconium lake whenever the solution contains $2 \cdot 10^{-6}$ g of zirconium per ml.

When a mixture of zirconium and platinum salts is agitated with an excess of a suspension of calcium carbonate, the platinum adsorbs to the precipitate, which takes on a cream-colored, even brownish hue. Inasmuch as the presence of a colored platinum ion would interfere with colorimetry, the precipitate had to be washed. This is done with hot water, and if the color of the percipitate is still yellow, it is dissolved in concentrated hydrochloric acid, neutralized with caustic soda, and again agitated with the carbonate suspension. Since much more platinum adsorbed to the precipitate when it was boiled, we resorted to precipitation of the zirconium at room temperature. The adsorption of platinum to the

precipitate is greatly increased at high concentrations of the platinum ion. A series of tests using various concentrations of platinum has shown that practically no platinum is adsorbed when the concentration of the latter is 1 g of platinum in 25-30 ml of solution.

In analyzing fused platinum, the weight of the sample of the melt must be such as to make the solution concentration no less than 10^{-5} g of zirconium per ml when the solution is colorimetrically analyzed in a 10-ml cyclinder. A sample weighing 10 g must be used, for example, when the melt contains, say, 0.001% Zr. At higher zirconium concentrations correspondingly smaller samples may be used. We established the correctness of the procedure used for determining zirconium in platinum by indirect standardization, mixing solutions of platinum and zirconium salts of known titers. We prepared a solution of platinic chloride by dissolving spongy or fused platinum in aqua regia, evaporating the solution twice with hydrochloric acid, and dissolving the residue in enough water to obtain a solution containing 1 g of platinum per 25 ml of solution. As a standard solution we used a solution of zirconium nitrate with a titer T = 10^{-4} g of zirconium per ml. The titer of the zirconium nitrate was ascertained gravimetrically, by precipitating the zirconium with ammonium hydroxide.

The results of our analysis of a mixture of solutions of platinum and zirconium salts containing 0.1% to 0.005% of zirconium are given in Table 1. Analyses were also made when shavingless colorimetric analysis for the zirconium in platinum was introduced into industrial practice (Tables 2 and 3).

TABLE 1

Used			Found	
Pt (g)	Zr (g)	Zr (%)	Zr (g)	Zr (%)
2	0.002	0.1	0.0019	0.095
3	0.0015	0.05	0.0014	0.047
3	0.0015	0.05	0.0016	0.053
3	0.001	0.033	0.0009	0.030
1	0.0002	0.02	0.00018	0.018
5	0.0005	0.01	0.00054	0.011
1	0.0001	0.01	0.00009	0.009
2	0.00016	0.008	0.00014	0.0070
3	0.00015	0.005	0.00016	0.0053
2	0.0001	0.005	0.00008	0.0040
1	0.0005	0.005	0.0004	0.0040
5	0.00025	0.005	0.00024	0.0048

TABLE 2

Shavingless Colorimetric Determination of Zirconium in Pure Salts

Zr used, g	Zr found, g
0.0003	0.00029
0.0003	0.00028
0.0002	0.00021
0.0002	0.00018
0.00018	0.00017
0.00007	0.00006
0.00002	0.000022
0.000017	0.000019
0.000015	0.000014
0.00001	0.00001

Determination procedure. 10 g of platinum is dissolved by heating it in aqua regia in a 400 ml porcelain beaker over a sand bath. The solution is twice evaporated with hydrochloric acid almost to dryness. The residue is dissolved in 200 ml of water and transferred to a 300 or 400-ml beaker; enough of a suspension of calcium carbonate is added to the solution to cover the

TABLE 3

Shavingless Colorimetric Determination of Zirconium in a Mixture of Zirconium and Platinum

Used			Found	
Pt (g)	Zr (g)	Zr (%)	Zr (g)	Zr (%)
1	0.0003	0.03	0.00028	0.028
1	0.0003	0.03	0.00028	0.028
1	0.0002	0.02	0.00016	0.016
1	0.0001	0.01	0.00007	0.007
1	0.0001	0.01	0.00008	0.008
5	0.00025	0.005	0.00023	0.0046
4	0.0003	0.0075	0.00028	0.0070

bottom of the beaker with a deposit 1 mm thick, and the whole is stirred with a (hand-operated or motor) stirrer for 1 hour at room temperature. After this stirring of the deposit, the whole is allowed to stand until the supernatant liquid is entirely clear, and then the latter is filtered through a double filter (white tape). At first the solution is dencated, and the deposit is washed repeatedly by decantation with hot water until the yellow color of the adsorbed platinum vanishes and the precipitate turns white. If not all the platinum is washed out, the deposit is dissolved in concentrated hydrochloric acid, sodium hydroxide is added until turbidity sets in, some more of the calcium carbonate suspension is added, and the whole is again stirred, allowed to stand, filtered, and washed until all the platinum is washed out (stannous chloride test). The washed precipitate is washed in hot hydrochloric acid (3:1); if the volume of the resultant solution exceeds 10 ml, it is evaporated and transferred quantitatively to the cylinder used for colorimetry. The solution is given a pH of about 2 by adding hydrochloric acid and sodium hydroxide (drop test with methyl violet in filter paper). A pipet is used to transfer 1 ml of a standard solution of zirconium nitrate with a $T = 10^{-4}$ of zirconium per ml, two drops of HCl (3:1), and 5 ml of water. If the test solution is somewhat yellowish, due to the adsorbed platinum, before the alizarin S is added, a few drops of platinic chloride are added to the standard solution until its color is the same as that of the test solution. Then one drop of alizarin S (0.04%) is added to each cylinder and the solutions are compared colorimetrically, adjusting the color of the liquid by dilution. If the color of the test solution is more intense than that of the standard solution, the volume of the test solution is increased to 10 ml, 1 ml of the resultant solution is taken up with a pipet and transferred to an empty cylinder, and colorimetry is continued until the same color is obtained as that of the standard solution. The solutions are stirred by blowing air through the liquid by means of a small glass tube, the end of which is drawn out into a capillary. The solutions are allowed to stand for 5 minutes, the volumes are read off, and the percentage of zirconium is calculated from the formula:

$$C_{Zr} = \frac{V_{test} \cdot T_{stand.}}{V_{stand.} \cdot P} \%$$

where V_{test} is the volume of the test solution; $V_{stand.}$ is the volume of the standard solution; $T_{stand.}$ is the titer of the standard solution; and P is the weight of the sample.

SUMMARY

1. The optimum acidity conditions have been determined for detecting minute quantities of zirconium by a reaction with sodium alizarinsulfonate, and the sensitivity of the reaction has been increased by flotation of the alizarin zirconium coordination compound with organic solvents.

2. A method has been developed for recovering minute quantities of zirconium from platinum by the action of suspensions of magnesium or calcium carbonate.

3. A shavingless colorimetric method has been developed for determining minute quantities of zirconium, ranging from 0.1% to 0.005% in fused platinum and it has been introduced into industry.

LITERATURE CITED

[1] Herman Liebhaisky and Winslow, J.Am.Chem.Soc., 60, 1776 (1938).
[2] T.A.Uspenskaya, E.I.Guldina, and M.S.Zverkova, Factory Lab. 9 (3), 142 (1940).
[3] J.H. de Boer, Rec. trav. Chim. Phys., 44, 1071 (1925).
[4] N.A.Tananaev, Prog. Chem., 5, (1941).
[5] N.A.Tananaev. The Shavingless Method. Metallurgy Press, Sverdlovsk (1948).

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THE LiCl-$BeCl_2$-H_2O SYSTEM AT 0°

A. V. Novoselova and I. G. Sosnovskaya

Lithium chloride reacts with many chlorides of divalent metals, forming double salts that crystallize from aqueous solutions.

Voskresenskaya and Yanatyeva [1] have produced the salt $LiCl \cdot MgCl_2 \cdot 7H_2O$. Basset and Sanderson [2], in their investigation of the LiCl – $CoCl_2$ – H_2O system, discovered several double salts: $LiCl \cdot CoCl_2 \cdot 2H_2O$; $7LiCl \cdot 2CoCl_2 \cdot 18H_2O$; $2CoCl_2 \cdot 3LiCl \cdot 6H_2O$ and, in a certain concentration range, solid solutions. Benrath [3] has also made a study of this system but found no solid solutions; according to that author the double salts of lithium chloride and cobaltous chloride are as follows: $CoCl_2 \cdot 4LiCl \cdot 10H_2O$; $CoCl_2 \cdot 2LiCl \cdot 4H_2O$; and $CoCl_2 \cdot LiCl \cdot H_2O$.

Benrath's researches [4] have shown that lithium chloride forms similar double salts with nickelous, manganous, and cuprous chlorides.

We were interested in the reaction of lithium chloride with beryllium chloride in water. The thermal analysis of the LiCl – $BeCl_2$ system made by Schmidt [5] has shown that the double salt $2LiCl \cdot BeCl_2$, which fuses with decomposition, is formed in that system. Lithium chloride crystallizes out of an aqueous solution with a varying amount of crystallization water, depending on the temperature.

Bogorodsky [6] made a systematic investigation of the hydrates of lithium chloride and found their transition points. According to him, $LiCl \cdot 2H_2O$ crystallizes below 21.5°, turning into $LiCl \cdot 3H_2O$ at -15°. In the interval between 21.5 and 98° $LiCl \cdot H_2O$ crystallizes, while above 98° anhydrous lithium chloride crystallizes out of the solution. The transition points of the hydrates of lithium chloride established by Bogorodsky were later confirmed by Hüttig and Reuscher [7] from measurements of vapor pressure. Voskresenskaya and Yanatyeva [1] in their investigation of the LiCl – H_2O system by the method of thermal analysis, discovered $LiCl \cdot 5H_2O$, formed below -57°, in addition to the hydrates specified above.

Bogorodsky [6] secured $LiCl \cdot 1.5H_2O$ from an aqueous-alcoholic solution. In their study of the $BeCl_2$ – H_2O system, Leikina and Novoselova [8] found that $BeCl_2 \cdot 4H_2O$ crystallized from an aqueous solution at 0, 20, 30, and 50°, while the dihydrate $BeCl_2 \cdot 2H_2O$ was found to be in equilibrium with the solutions at 75°.

Preparation of the initial substances and their analyses. We prepared beryllium chloride by dissolving pure beryllium hydroxide in concentrated hydrochloric acid, filtering the solution through a glass filter, and evaporating it over a water bath to a syrupy consistency. Hydrogen chloride was passed through the solution, chilled with snow. After the hydrogen chloride had been passed through for a long time, a copious precipitate of the tetrahydrate of beryllium chloride settled out as well-shaped needles.

The crystals of beryllium chloride were filtered out, dried in a desiccator above sulfuric acid, and analyzed for their beryllium and chlorine content. The samples of beryllium chloride used for analysis were weighed in boxes containing water in order to avoid any loss of hydrochloric acid, as a result of hydrolysis

of the beryllium chloride. The percentage of beryllium in the preparation was determined as BeO. The chlorine was determined by the Volhard method.

Found %: Be 5.99; Cl 46.33. $BeCl_2 \cdot 4H_2O$. Computed %: Be 5.90; Cl 46.32.

Lithium chloride was prepared from pure lithium carbonate by dissolving the latter in hydrochloric acid. The crystals of lithium chloride obtained after the solution had been evaporated were dried in a desiccator above sulfuric acid.

Microscopic examination of the lithium chloride we had prepared indicated that the preparation was a mixture of the mono- and dihydrates. $LiCl \cdot H_2O$ crystallizes as well-formed octahedra, which extinguish light when crossed with nicols in the polariscope; they can be readily distinguished from the prismatic crystals of $LiCl \cdot 2H_2O$, which exhibit double refraction.

We determined the percentage of lithium in the lithium chloride as $LiSO_4$, while the chlorine was determined by titration with silver nitrate and fluorescin.

Found %: Li 9.97; Cl 51.27; H_2O 38.76 (by difference); Li:Cl = 0.99:1.
$LiCl \cdot H_2O$ Computed %: Li 11.49; Cl 58.71; H_2O 29.80.
$LiCl \cdot 2H_2O$ computed %: Li 8.85; Cl 45.24; H_2O 45.91.

Analysis corroborated that the preparation is a mixture of the mono- and dihydrates.

Analysis of the solution in the solid phases. The percentage of lithium in the solution of pure lithium chloride was determined as the sulfate. A solution, saturated with beryllium chloride, was analyzed in different ways:

1. Beryllium hydroxide was precipitated with ammonia, desiccated, and calcined.

2. The chlorine was determined by titration with silver nitrate by the Volhard method.

3. The solution of beryllium nitrate was titrated with alkali and phenolphthalein. The beryllium chloride was hydrolyzed in aqueous solution, and the resulting hydrochloric acid could be determined quantitatively; then the percentage of beryllium chloride in the solution could be calculated.

When the chlorine is determined by titration with silver nitrate, using an adsorption indicator, the results are more accurate than in a Volhard titration, but titration with fluorescin requires that the solutions used be neutral, whereas the solutions that contained beryllium chloride were acid. That is why we used the Volhard method of titration in determining solubility in our first experiments. In our subsequent determinations of chlorine in the solutions we titrated after neutralization with alkali. This enabled us to titrate the chlorine with silver nitrate and fluorescin. We analyzed solutions that contained both lithium chloride and beryllium chloride as follows: The total chlorine was determined in one sample of the solution by titration with silver nitrate, while another sample of the solution was titrated with alkali and phenolphthalein, which enabled us to determine the percentage of beryllium chloride in the solution. The results of the two titrations enabled us to calculate the percentage of lithium and beryllium chlorides in the solution. To secure definite proof of the applicability of such a method of determination to our mixture of salts, we prepared artificial mixtures, containing known quantities of LiCl and $BeCl_2$, and titrated these mixtures with sodium hydroxide and phenolphthalein and silver nitrate by the Volhard method. We found that when the salt mixture was titrated, the quantity of sodium hydroxide consumed was equivalent to the percentage of beryllium chloride alone in the mixture, the lithium chloride not being titrated

with sodium hydroxide. Titration with silver nitrate gives the aggregate percentage of chlorine, combined with beryllium and with lithium.

The results of our investigations of solutions of pure salts and of their mixtures are given in Table 1.

TABLE 1

Expt. No.	Substances tested	Weight, g	Used for analysis, ml	Consumption		Chlorine found, g		Chlorine content, g, in salt mixture	
				$AgNO_3$, 0.1 N, ml	NaOH, 0.1 N, ml	Volhard method	Titration with alkali	Calc.	Found
1	$LiCl \cdot nH_2O$ ..	0.4520 (in 50 ml)	10	12.95	-	0.04592	-	-	-
2	$BeCl_2 \cdot nH_2O$.	0.8559 (in 100 ml)	10	10.43	10.42	0.03698	0.03695	-	-
3	LiCl + $BeCl_2$ (10 ml each of solutions used in Tests 1 and 2)	-	20	23.41	10.43	0.0830	0.03698	0.0829	0.0830

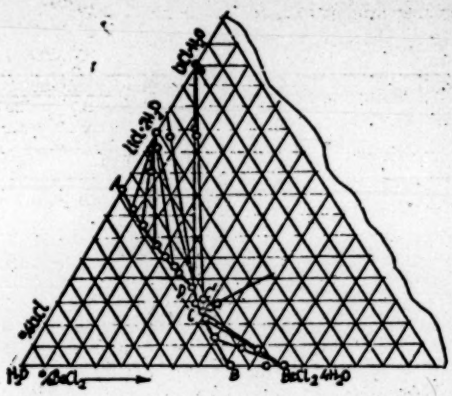
Study of solubility in the LiCl - $BeCl_2$ - H_2O system. Solubility was investigated in a thermostat filled with melting ice. A solution containing an excess of the salt was placed in a glass test tube fitted with an oil seal and stirred mechanically. It took 2-3 days for equilibrium to be attained. Samples of the solution were taken for analysis by means of pipets fitted with glass filters. Samples of the solid phase were separated from the motherliquor in a funnel fitted with a glass filter, the filter and the crystals on it being chilled with snow during suction filtering. The composition of the solid phases was determined by the Schreinemakers residue method.

TABLE 2

Expt. No.	Composition of solution, % by weight			Composition of residue, % by weight			Bottom phases
	LiCl	$BeCl_2$	H_2O	LiCl	$BeCl_2$	H_2O	
1	41.32	-	56.68	54.03	-	45.97	
2	36.57	4.73	58.70	51.11	0.36	48.53	
3	33.58	7.49	58.93	52.84	1.24	45.92	
4	27.56	13.48	58.96	51.66	2.84	45.50	$LiCl \cdot 2H_2O$
5	25.88	16.22	57.90	48.39	3.00	48.61	
6	23.72	18.23	58.05	46.92	3.51	49.57	
7	20.05	22.80	57.15	44.89	4.83	50.28	
8	17.20	25.80	57.00	54.20	2.31	43.49	$LiCl \cdot 2H_2O$ + $LiClH_2O$
9	15.52	27.20	57.28	20.57	28.34	51.09	$LiCl \cdot 2H_2O$+$BeCl_2 \cdot 4H_2O$ *
10	13.80	28.01	58.19	55.00	7.02	37.98	$LiCl \cdot H_2O$
11	13.30	29.50	57.20	53.71	7.71	38.58	$LiCl \cdot H_2O$ + $BeCl_2 \cdot 4H_2O$
12	13.36	29.43	57.21	14.20	33.31	52.49	
13	12.30	30.70	57.00	-	-	-	
14	11.12	31.28	57.60	3.6	45.04	51.36	$BeCl_2 \cdot 4H_2O$
15	5.74	34.50	59.76	4.15	41.92	53.93	
16	-	40.35	59.65	-	48.17	51.83	

* Metastable solution.

The results of our investigation of the $LiCl - BeCl_2 - H_2O$ system are listed in Table 2 and plotted in the triangular diagram. Our measurements indicate that the solubility of lithium chloride at 0° is 41.32 g per 100 g of solution (Point A in the diagram). $LiCl \cdot 2H_2O$ is in equilibrium with the solution at that temperature. The solubility of beryllium chloride at 0° was found to be 40.35 g per 100 g of solution (Point B in the diagram).



$LiCl - BeCl_2 - H_2O$ system at 0°.

After having determined the solubility of lithium chloride in the presence of increasing quantities of beryllium chloride, we secured a terminal solution saturated with both salts: lithium chloride dihydrate and beryllium chloride tetrahydrate. This solution is indicated by Point C' in the diagram; when we tried to secure a solution of the same composition by starting with a solution saturated with beryllium chloride and increasing the concentration of lithium chloride progressively, we secured a solution saturated with $LiCl \cdot H_2O$ and $BeCl_2 \cdot 4H_2O$, the composition of which is indicated by Point C in the diagram. Adding lithium chloride dihydrate to this solution and stirring it for another three days produced no change in its composition. When we examined the solid phase under the microscope, we found no lithium chloride dihydrate in it. This indicates that the monohydrate of lithium chloride (in addition to the beryllium chloride tetrahydrate) rather than the dihydrate is the stable phase in a solution whose composition is that denoted by Point C. We believe that Point C' in the diagram represents a metastable equilibrium.

The composition of the solutions represented by Points C and C' in the diagram is given in the following table.

	Per cent LiCl	Per cent $BeCl_2$	Solid phases
Solution C:	13.3	29.4	$LiCl \cdot H_2O + BeCl_2 \cdot 4H_2O$
Solution C':	15.52	27.2	$LiCl \cdot 2H_2O + BeCl_2 \cdot 4H_2O$

In the solution whose composition is given by C, the stable phase is lithium chloride monohydrate; hence, it may be assumed that Point C is the transition point from the dihydrate to the monohydrate for any solution concentration up to that point.

We did not find this point at first when we traced the solubility branch AC.

After having discovered that the solution is metastable at Point C', we repeated our investigation of the solubility line AC and found the transition point of $LiCl \cdot 2H_2O$ to $LiCl \cdot H_2O$ (Point D in the diagram) at a solution composition of 25.8% $BeCl_2$ and 17.2% LiCl. We found $LiCl \cdot H_2O$ in the solid phase when the solution contained 28% $BeCl_2$ and 13.8% LiCl.

These tests lead us to believe that there are two monovariant equilibria that are stable in the LiCl – $BeCl_2$ – H_2O system at 0°: 1) an equilibrium of the solution with the solid phases $LiCl \cdot 2H_2O$ and $LiCl \cdot H_2O$ (Point D); and 2) an equilibrium of the solution with the solid phases $LiCl \cdot H_2O$ and $BeCl_2 \cdot 4H_2O$ (Point C).

The equilibrium of the solution with the solid phases $LiCl \cdot 2H_2O$ and $BeCl_2 \cdot 4H_2O$ is metastable at 0°.

SUMMARY

1. The solubility isotherm of the LiCl – $BeCl_2$ – H_2O system has been investigated at 0°.

2. No double salts are formed in this system at 0°. The following crystal hydrates may exist in equilibrium with the solutions: $LiCl \cdot H_2O$, $LiCl \cdot 2H_2O$, and $BeCl_2 \cdot 4H_2O$.

LITERATURE CITED

[1] N.K.Voskresenskaya and O.K.Yanatyeva, Bull. USSR Acad. Sci., 1937, 1, 97.

[2] Basset and Sanderson, J.Chem.Soc., London, 1932, 1855.

[3] Benrath, Z. allgem. anorg. Chem. 163, 396 (1927).

[4] Benrath, Z. allgem. anorg. Chem., 205, 417 (1932); 220, 145 (1934).

[5] Schmidt, Ann. Chim., (10) 1, 367 (1929).

[6] A.Ya.Bogorodsky, J.Russ.Phys.Chem.Soc., 25, 316 (1893); 26, 209 (1894); 43, 1286 (1911).

[7] Huttig and Reuscher, Z. allgem. anorg. Chem., 137, 155 (1924).

[8] B.N.Leikina and A.V.Novoselova, J.Gen.Chem. 7, 241 (1937).

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SURFACE TENSION AND TOTAL SURFACE ENERGY OF RATIONAL BINARY LIQUID SYSTEMS

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Continuing our research on the experimental evidence for the ten geometrically possible theoretical types of surface tension isotherms of rational binary liquid systems, we have made a study of four systems with an upper singular point (in the terminology adopted by one of the present authors) [1].

EXPERIMENTAL

Procedure. The surface tension was measured by Cantor's method [2] as modified by Rebinder [3], several auxiliary devices [4,5] being added to the apparatus. The capillary tip was set at the gas – liquid interface by means of a micrometer screw. A large oil thermostat, equipped with a mercury thermoregulator that enabled us to keep the temperature constant within ± 0.1°, was used in our surface-tension measurements. The relative experimental error did not exceed 0.2%.

Results of measurement. We made a study of systems consisting of mustard oils and primary or secondary amines, as typical representatives of rational systems.

The results of our investigations of the various systems are listed below.

1. Allyl mustard oil – ethylaniline system. This system is one of those on which the most work has been done, and many of its properties have been determined [6-8]. These properties indicate that it is a rational system. The constituents were purified as follows. The ethylaniline was purified with potassium hydroxide, distilled at 202-203°, and then distilled at reduced pressure;

$$d_4^{25} = 0.9578;\ n_D^{20} = 1.5552.$$

The allyl mustard oil was desiccated for a long time above calcium chloride, then distilled at 147-147.5°, and then distilled in vacuum;

$$d_4^{20} = 1.0138;\ n_D^{20} = 1.5204.$$

The constituents reacted together very slowly, several days being required for equilibrium to be reached. This may be utilized in the study of the kinetics of formation of rational systems. In view of the slowness with which allylethylphenylurea was formed, we allowed the solutions to stand for several days after they had been prepared, keeping them at 70° for 2 hours before making measurements. The reaction was judged to be complete when the refractive index remained constant. The results of our measurements of surface tension in ergs/cm^2 at 25, 50, and 75° are given in Table 1 and Fig. 1.

As we see from Table 1, each of the $\sigma_{(c)}$ isotherms of the system consist of two branches that intersect at a singular maximum, the composition of which does not vary with temperature, being exactly 50 mol. % of each constituent. Hence, the compound that is formed (allylethylphenylurea) is not dissociated thermally in the liquid phase. The deviations of the $\sigma_{(c)}$ isotherms from the additive

TABLE 1

Allyl Mustard Oil – Ethylaniline System

Expt. No.	$C_6H_5NHC_2H_5$, Mol. %	$\sigma_{25°}$	$\sigma_{50°}$	$\sigma_{75°}$	$\gamma_{25-50°}$	$U_{25°}$	$U_{50°}$	$U_{75°}$
1	00.00	33.93	30.86	27.87	0.0035	70.03	69.94	69.97
2	20.00	35.51	33.22	30.79	0.0027	63.67	63.58	63.50
3	40.00	39.44	36.72	34.20	0.0026	70.73	70.63	70.74
4	45.00	40.52	37.72	35.65	0.0024	69.42	69.51	69.40
5	48.00	40.92	38.18	35.93	0.0024	70.70	70.68	70.75
6	50.00	41.20	38.37	36.10	0.0024	71.59	71.48	71.59
7	52.00	40.89	37.90	35.85	0.0025	70.98	70.88	70.99
8	55.00	40.25	37.67	35.27	0.0025	69.75	69.64	69.72
9	60.00	39.45	37.02	34.44	0.0026	69.25	69.32	69.20
10	80.00	37.61	35.31	32.55	0.0027	67.71	67.93	67.69
11	100.00	36.84	34.22	31.46	0.0029	69.32	69.42	69.39

straight lines at the singular points were: 16.4% at 25°; 17.9% at 50°; and 21.7% at 75°. As we see, these deviations increase with temperature; furthermore, this is true of all the rational systems we have investigated, as will be shown later on. It should be noted that whereas the isotherm branch on the amine side is slightly concave upward throughout, the branch on the oil side has a point of inflection, indicating that there is no reaction between the amine and the thiourea, but that a reaction does take place between the latter and the oil. This is illustrated rather sharply in other systems of mustard oils and amines. The conclusion, however, that the temperature coefficient of the surface tension may be utilized for physico-chemical analysis requires detailed investigation. For rational systems, however, as we have been able to demonstrate for systems consisting of mustard oils and amines, the curve of the relative temperature coefficient as a function of the composition passes through a minimum. This minimum is located at the composition of the resultant compound.

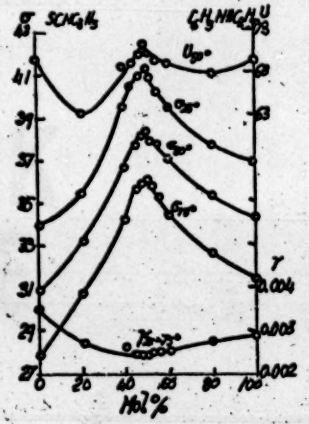

Fig. 1.

Table 1 gives the values of the relative temperature coefficient as a function of the composition, as calculated from the equation:

$$\gamma = \frac{1}{\sigma_1} \frac{\sigma_1 - \sigma_2}{t_2^\circ - t_1^\circ} ,$$

where σ_1 and σ_2 are the values of the surface tension at the temperatures t_1° and t_2°; and γ is the relative temperature coefficient.

The $\gamma(c)$ curve (bottom curve in Fig. 1) passes through a minimum. The limiting isotherm of surface tension (at the temperature of -273°) might be termed the curve of the total surface energy. We calculated the latter from the Gibbs-Helmholtz equation:

$$U = \sigma - T\frac{d\sigma}{dT},$$

where U is the total surface energy; σ is the free surface energy (surface tension); and $d\sigma/dT$ is its temperature coefficient. The numerical values of the total surface energy (Table 1) indicate that it is independent of temperature. The curve $U_{(c)}$ (top curve in Fig. 1) has a singular maximum, corresponding to the composition of the compound.

Other systems containing mustard oils and amines. All the systems enumerated below, containing mustard oils and primary or secondary amines, have physicochemical properties that are essentially similar, qualitatively speaking, to those of the system just considered, differing only quantitatively.

2. Phenyl mustard oil – diethylamine system. The density and viscosity [10] and the refractive index [11] of this system have been investigated. The diethylamine was prepared by distillation, the fraction boiling at 55.7-56° being used.

$$d_4^{20} = 0.7108; \quad n_D^{20} = 1.3876.$$

Its surface tension was measured for every 10° between 0 and 50°, the polytherm

$$\sigma = 22.49 - 0.112\ t^\circ$$

being secured, where σ is the surface tension at the temperature t°; the constant term is its value at 0°; and the coefficient of t° is the temperature coefficient of the surface tension.

The phenyl mustard oil was desiccated for a long time above metallic sodium, then it was distilled at 218-218.5°, and finally distilled at reduced pressure:

$$d_4^{25} = 1.1282; \quad n_D^{22} = 1.6492.$$

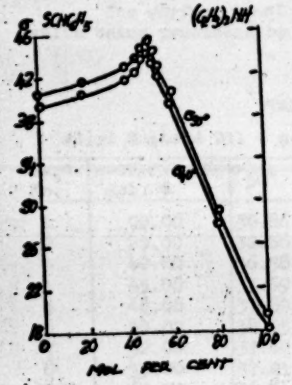

Fig. 2.

TABLE 2

Phenyl Mustard Oil – Diethylamine System

Expt. No.	$(C_6H_5)_2NH$ Mol. %	σ_{30°	σ_{40°	$\gamma_{30\text{-}40^\circ}$	U_{30°	U_{40°
1	00.00	40.48	39.31	0.0030	75.93	75.93
2	20.00	41.45	40.28	0.0029	76.90	76.90
3	40.00	42.89	41.70	0.0028	78.94	78.93
4	45.00	43.50	42.32	0.0028	79.25	79.25
5	48.00	44.90	43.75	0.0027	79.75	79.75
6	50.00	45.18	44.02	0.0026	80.32	80.32
7	52.00	44.22	43.10	0.0026	78.15	78.15
8	55.00	43.01	41.88	0.0027	77.24	77.25
9	60.00	40.62	39.44	0.0030	76.37	76.37
10	80.00	29.02	27.85	0.0042	64.47	64.47
11	100.00	19.43	18.24	0.0065	55.48	55.48

The constituents combined with the evolution of considerable heat. The constituents were mixed together in double-elbow vessels with ground-glass stoppers, chilled with ice, to prevent decomposition of the resultant diethylphenylthiourea and eventual evaporation of the diethylamine.

The solutions prepared in this manner were nearly colorless.

Inasmuch as the viscosity of the mixture was rather high at 30-40°, it took 40 to 50 seconds for each bubble to form. We therefore measured the static surface tension, which fully agreed with the equilibrium absorption layer established with time.

The results of our measurements of $\sigma_{(c)}$ at 30° and 40° are given in Table 2 and Fig. 2.

The deviations of the experimental isotherm from additivity at the singular points were: 50.3% at 30° and 52.9% at 40°; i.e., they were somewhat greater than the corresponding deviations for the preceding system investigated. We are inclined to attribute this to the fact that the resultant compound not only is not dissociated thermally into its constituents, but is actually associated.

The values of the relative temperature coefficient and the total surface energy are listed in Table 2 and shown in Fig. 3. The singular form of the $U_{(c)}$ curve is quite obvious.

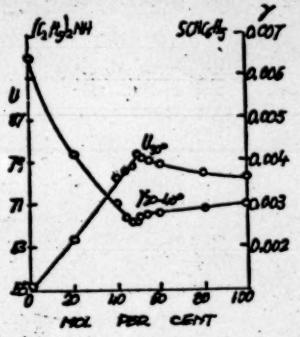

Fig. 3.

3. Allyl mustard oil – metatoluidine system. No research has been done hitherto on any of the properties of this system. The metatoluidine was desiccated above potassium hydroxide, then distilled at 199-199.5°, and finally distilled at reduced pressure:

$$d_4^{20} = 0.9987; \quad n_D^{20} = 1.5709.$$

Its surface tension was measured at 10° intervals from 0 to 150°, the results being processed by the method of least squares, yielding the polytherm:

$$\sigma = 40.16 - 0.094\,t°.$$

TABLE 3

Allyl Mustard Oil – m-Toluidine System

Expt. No.	m-$CH_3C_6H_4NH_2$ mol. %	$\sigma_{50°}$	$\sigma_{75°}$	$\gamma_{50-75°}$	$U_{50°}$	$U_{75°}$
1	00.00	30.86	28.37	0.0045	71.24	71.24
2	20.00	32.66	30.59	0.0033	65.93	65.92
3	40.00	36.58	34.70	0.0027	67.58	67.58
4	45.00	37.69	35.66	0.0028	70.31	70.30
5	48.00	37.89	35.96	0.0027	69.22	69.23
6	50.00	38.25	36.24	0.0027	70.55	70.54
7	52.00	37.60	35.54	0.0028	70.87	70.87
8	55.00	37.21	35.22	0.0028	69.19	69.18
9	60.00	36.54	34.46	0.0030	70.13	70.13
10	80.00	35.60	33.51	0.0031	69.19	69.12
11	100.00	35.51	33.42	0.0031	69.10	69.08

The only measurement of the surface tension of metatoluidine to be found in the literature was made by Richards [12], who found $\sigma_{20°} = 36.9 \pm 0.3$. Calculation readily shows that our value, $\sigma_{20°} = 38.29$, lies between the respective values for the ortho and para isomers as is usually the case for σ, whereas Richards' value lies below these values.

The results of our measurement of $\sigma_{(c)}$ at 50 and 70° are given in Table 3 and Fig. 4. The form of the surface tension isotherms is similar to those of the isotherms for the preceding systems.

The deviations of the $\sigma_{(c)}$ isothemrs from additivity at the singular

points were: 15.3% at 50° and 17.3% at 70°. The numerical values of the relative temperature coefficient and of the total energy are given in Table 3 and plotted in Fig. 4.

4. Phenyl mustard oil – aniline system. We have been unable to find any data on this system in the literature.

The aniline was successively desiccated above potassium hydroxide and metallic sodium, after which it was distilled, the 183.5-184° fraction being taken for our use;

$$d_4^{20} = 1.0221;\ n_D^{20} = 1.5866,$$

It was redistilled before use. The system was investigated at 140 and 150°.

The data on the surface tension its temperature coefficient, and the total surface energy are given in Table 4 and Fig. 5.

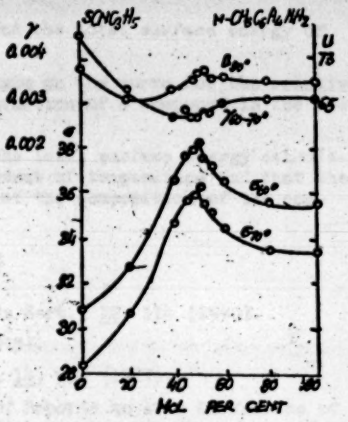

Fig. 4.

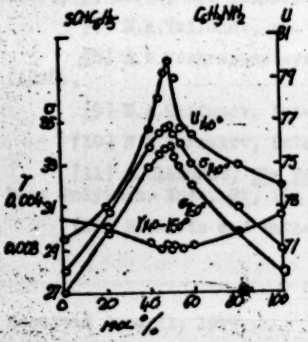

Fig. 5.

TAVLE 4.

Phenyl Mustard Oil – Aniline System.

Expt. No.	$C_6H_5NH_2$ mol. %	$\sigma_{140°}$	$\sigma_{150°}$	$\gamma_{140-150°}$	$U_{140°}$	$U_{150°}$
1	00.00	28.14	27.09	0.0038	71.50	71.49
2	20.00	30.82	29.80	0.0034	72.94	72.94
3	40.00	33.87	32.83	0.0032	76.82	76.82
4	45.00	34.45	33.39	0.0031	78.22	78.22
5	48.00	34.76	33.68	0.0032	79.36	79.36
6	50.00	34.86	33.77	0.0032	79.87	79.87
7	52.00	34.39	33.31	0.0032	78.99	78.99
8	55.00	33.96	32.93	0.0031	76.50	76.49
9	60.00	33.01	31.96	0.0032	76.37	76.37
10	80.00	30.88	29.81	0.0035	75.07	75.07
11	100.00	29.05	27.96	0.0037	74.06	74.06

The deviation of the experimental $\sigma_{(c)}$ isotherms from additivity at the singular points were: 21.8% at 140° and 22.50% at 150°.

The markedly singular form of the curve representing the total surface energy is worthy of note.

SUMMARY

1. A study has been made of the surface tensions of four systems constituted by mustard oils and primary or secondary amines at various temperatures.

2. It has been shown that they all display the first type of isotherms of surface tension, for rational binary liquid systems.

3. The relative temperature coefficient and the total surface energy of these systems have been calculated.

4. It has been shown that there is a minimum on the curve for the relative temperature coefficient, which represents the formation of a compound in the system.

5. It has been shown that the values of the total surface energy calculated from the Gibbs-Henholtz equation are independent of temperature and that the $U_{(c)}$ curve possesses a singular maximum located at the composition of the compound.

LITERATURE CITED

[1] N.A.Trinov, Bull. Phys.Chem., Analysis Sect., 12, 114 (1940).

[2] E.Schrodinger, Ann. Phys. 46, 413 (1915).

[3] P.A.Rebinder, J.Expt. Biol. and Med., 14, 939 (1927).

[4] O.A.Osipov and N.A.Trifonov, Theses of Reports to 10th Conference of Young Scientists of Rostov State Univ., 22 (1940).

[5] S.P.Miskidzhyan and N.A.Trifonov, J.Gen.Chem. 17, 1231 (1947).

[6] N.A.Trifonov and K.N.Samarina, Bull. Inst. Biol. Research, Perm State Univ., 6, No. 6, 291 (1929).

[7] N.A.Trifonov, op. cit., 6, No. 5, 247 (1928).

[8] N.K.Voskresenskaya, Sci. Rep., Saratov State Univ., 6, No. 3, 227 (1928).

[9] N.A.Trifonov, Nature (USSR), 11, 38 (1934).

[10] N.S.Kurnakov, Selected Works, I, 214. Leningrad (1938).

[11] A.Glazunov, The Refractive Index of Binary Systems. Bull. St. Petersburg Polytech. Inst. 21, 291 (1914).

[12] Richards and Mathews, J.Am.Chem.Soc., 30, 8 (1908).

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A PHYSICOCHEMICAL STUDY OF THE SYSTEMS:

IODINE CHLORIDE-SUBSTITUTED ACID AMIDES

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This paper represents a continuation of our research on systems consisting of iodine halides and acid amides. In our preceding reports [1,2,3] we have described the results of our research on the ICl – CH_3CONH_2 and ICl – $C_6H_5CONH_2$ systems by the methods of thermal analysis, viscosity, conductance, electrolysis, and ion transfer. These researches enabled us to establish the existence of several new coordination compounds and to recover some of them in their individual states. It has been shown that all of these compounds of iodine chloride and acid amides are rather strong electrolytes containing a complex cation that is an addition product of the I^+ ion and the acid amide. Compounds of equimolar composition were found to have the structure of $[RCONH_2 \cdot I]Cl$. The following tautomeric change is known to occur in acid amides:

We were interested in learning which of these two forms – amidic or imidic – of the acid amides react with iodine chloride. To answer this question we proposed to make a study of those derivatives of the acid amides in which one or both of the hydrogen atoms in the amide group was replaced by a hydrocarbon radical. The tautomeric change ought to be much weaker in such substances, being altogether impossible in disubstituted compounds of the general formula $RCON(R_1)_2$. With this as our goal, we investigated systems consisting of iodine chloride and diethylbenzamide $C_6H_5CON(C_2H_5)_2$ or acetanilide $C_6H_5NHCOCH_3$.

1. ICl – $C_6H_5CON(C_2H_5)_2$ System

The diethylbenzamide was synthesized from benzoyl chloride and diethylamine [4]. An ethereal solution of the diethylbenzamide was kept for several days above anhydrous calcium chloride, after which the ether was driven off, and the residue was distilled twice, the 281-282° fraction being used. According to the literature, diethylbenzamide boils at 282°. The preparation we had synthesized was a colorless, oily liquid.

The iodine chloride was prepared as described in previous reports from our laboratory [5].

The mixing of diethylbenzamide and iodine chloride involves the evolution of considerable heat. The process of crystallization of these mixtures is extremely slow and involves appreciable supercooling, which made the thermal analysis of the system extremely difficult and made it impossible to secure reliable results. We therefore resorted to other methods of physicochemical analysis: determining the viscosity, the conductance, and other properties.

The viscosity of the system was measured by the method and with the apparatus described in our previous reports [6]. The results of our viscosity

asurements are given in Table 1 and Fig. 1.

TABLE 1

Viscosity of the ICl – $C_6H_5CON(C_2H_5)_2$ System

Mol % of $C_6H_5CON(C_2H_5)_2$	Viscosity, centipoises	
	35°	50°
100.00	5.808	2.870
83.64	9.767	4.379
75.75	15.129	5.871
64.29	39.214	11.112
51.72	53.452	18.162
47.77	53.096	17.849
42.29	36.124	14.882
36.35	29.991	10.004
30.48	15.687	7.889
0.00	3.052	2.015

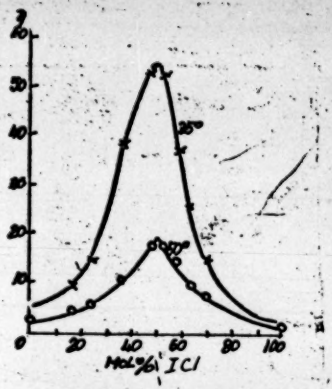

Fig. 1. Viscosity of the ICl – $C_6H_5CON(C_2H_5)_2$ system.

The sepcific gravities of the ICl – $C_6H_5CON(C_2H_5)_2$ system, required for calculating the viscosity and the molecular conductance, were obtained by interpolation from our experimental data (Table 2). The specific gravity of the ICl – $C_6H_5CON(C_2H_5)_2$ system was determined in a dilatometer type of vessel, with a widened space at the top of the capillary.

The data in Table 1 and Fig. 1 indicate that the viscosity isotherms of the ICl – $C_6H_5CON(C_2H_5)_2$ system possess a maximum, the position of which does not shift with temperature.

The viscosity maximum occurs at the equimolar proportion of the constituents, which is evidence that a coordination compound $C_6H_5CON(C_2H_5)_2 \cdot ICl$ is formed. This is also borne out by the change in the temperature coefficient of viscosity with the concentration of the system, as seen in Fig. 1.

TABLE 2

Specific Gravity of the ICl – $C_6H_5CON(C_2H_5)_2$ System

Mol. % of ICl	Specific gravity	
	35°	50°
100.00	3.192	3.166
64.75	1.985	1.900
46.12	1.600	1.521
36.45	1.405	1.358
0.00	1.071	1.023

Conductance of the ICl – $C_6H_5CON(C_2H_5)_2$ system and of its nitrobenzene solution. The results of our measurements of the specific conductance of the ICl – $C_6H_5CON(C_2H_5)_2$ system are given in Table 3 and in Fig. 2. As we see, the conductance isotherms of the ICl – $C_6H_5CON(C_2H_5)_2$ system have the usual shape for this type of system, the conductance at first rises sharply as the concentration of diethylbenzamide is increased, reaching a maximum of $2.3 \cdot 10^{-2}$ $ohm^{-1}cm^{-1}$ (35°) or $3.1 \cdot 10^{-2}$ $ohm^{-1}cm^{-1}$ (at 50°) at 8 mol. % of $C_6H_5CON(C_2H_5)_2$, after which it drops just as sharply to a value of $0.4\text{-}0.9 \cdot 10^{-3}$ $ohm^{-1}cm^{-1}$ at a composition of the system that approaches the equimolecular. Thereafter the conductance isotherms run nearly parallel to the axis of abscissas.

The molecular conductance of the ICl – $C_6H_5CON(C_2H_5)_2$ system was calculated from the specific conductance and the specific gravity (Table 4 and Fig. 3). As we see from the figure, the curve of molecular conductance, based on

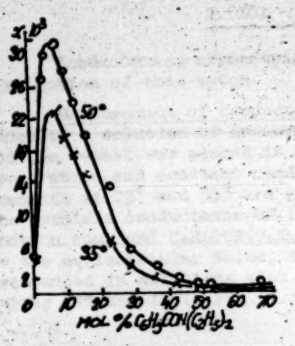

Fig. 2. Specific conductance of the ICl – $C_6H_5CON(C_2H_5)_2$ system.

TABLE 3

Specific Conductance of the ICl – $C_6H_5CON(C_2H_5)_2$ System

Mol. % $C_6H_5CON(C_2H_5)_2$	Specific conductance, $\kappa \cdot 10^3$	
	35°	50°
4.25	19.80	27.03
5.48	–	30.00
8.07	22.97	31.00
10.47	19.40	27.94
12.99	17.42	23.71
16.81	14.57	19.61
22.79	6.30	13.28
28.68	3.443	5.439
36.05	1.959	3.389
46.38	0.913	1.713
48.02	0.457	1.057
52.39	0.480	0.896
66.95	0.400	0.815
81.53	0.392	0.752

TABLE 4

Molecular conductance of the ICl – $C_6H_5CON(C_2H_5)_2$ System at 50°

Mol.% of diethyl-benzamide	φ_1 (ml)	φ_2 (ml)	μ_1	μ_2
4.25	57.94	1290.0	1.56	34.88
5.48	58.82	1014.9	1.76	30.45
8.07	66.46	689.1	2.06	21.36
10.47	67.55	577.8	1.86	16.15
12.99	72.25	484.20	1.71	11.48
16.81	79.83	395.22	1.56	7.75
22.79	93.10	315.53	1.24	4.19
26.68	108.62	270.16	0.591	1.47
36.05	133.06	236.13	0.451	0.800
46.38	167.65	227.97	0.287	0.390
48.02	189.92	205.64	0.201	0.217
52.39	219.09	199.12	0.196	0.178
66.95	285.76	190.51	0.314	0.155
81.53	775.91	175.77	0.583	0.132

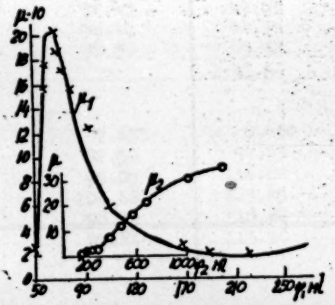

Fig. 3. Molecular conductance of the ICl – $C_6H_5CON(C_2H_5)_2$ system at 50°.

μ_1) $C_6H_5CON(C_2H_5)_2$ as the solvent; μ_2) ICl as the solvent.

ICl as the electrolyte ($\varphi_1 - \mu_1$) has a typical "anomalous" shape, the minimum molecular conductance occurring at the equimolecular proportion of the constituents; this latter is obviously nothing but the actual conductance of the coordination compound $C_6H_5CON(C_2H_5)_2 \cdot ICl$ (in the liquid state). The isotherm of molecular conductance, based on $C_6H_5CON(C_2H_5)_2$ as the electrolyte ($\varphi_2 - \mu_2$), is

* φ_1 and μ_1 are based on ICl as the electrolyte; φ_2 and μ_2 are based on $C_6H_5CON(C_2H_5)_2$ as the electrolyte.

resented by a curve of the usual type; the conductance increases with dilution.

2. ICl – $C_6H_5CON(C_2H_5)_2$ – $C_6H_5NO_2$ System

Conductance, cryoscopic, and ion-transfer methods were employed in the investigation of this sytem.

Measurement of conductance. Increasing quantities of $C_6H_5CON(C_2H_5)_2$ were added to a solution of iodine chloride in nitrobenzene, the mixture was stirred, and the vessel was placed in a thermostat for 20-25 minutes to reach a constant temperature and constant conductance of the solution. The results of our measurements at 25° and 35° are given in Table 5 and Fig. 4. These data show that the specific conductance of this system rises with the concentration of the coordination compound $C_6H_5CON(C_2H_5)_2 \cdot ICl$, i.e., as the $C_6H_5CON(C_2H_5)_2$:ICl ratio rises to the equimolecular value, after which it begins to drop. This phenomenon is pronounced in solutions with higher concentrations of ICl (second series of tests, Curves III and IV in Fig. 4.

TABLE 5

Specific Conductance of the ICl – $C_6H_5CON(C_2H_5)_2$ – $C_6H_5NO_2$ System

$C_6H_5NO_2$, grams	ICl, grams	$C_6H_5CON(C_2H_5)_2$, grams	$C_6H_5CON(C_2H_5)_2$ · ICl + n in mol. %	Specific conductance, $\kappa \cdot 10^5$ 25°	35°
25.8161	0.4434	–	0.00	4.841	5.640
25.8161	0.4434	0.0644	11.75	12.68	17.91
25.8161	0.4434	0.1522	23.93	25.59	29.39
25.8161	0.4434	0.2796	36.64	34.43	41.83
25.8161	0.4434	0.4489	48.15	38.44	44.76
25.8161	0.4434	0.6004	54.51	38.59	45.32
25.8161	0.4434	0.8168	62.82	–	45.91
			Second Series		
10.4750	1.2013	–	0.00	7.673	8.630
10.4750	1.2013	0.4333	24.86	82.50	94.33
10.4750	1.2013	1.0904	45.40	95.05	116.80
10.4750	1.2013	1.3722	51.16	104.66	123.45
10.4750	1.2013	1.7825	57.64	98.92	118.80
10.4750	1.2013	2.1184	61.80	95.84	113.50

Cryoscopy of the ICl – $C_6H_5CON(C_2H_5)_2$ system in nitrobenzene. A known quantity of nitrobenzene was placed in a container used for cryoscopic measurements, and its freezing point was determined with a Beckmann thermometer, after which a known quantity of iodine chloride was added, and the freezing point of the solution (t_0) was determined. Then increasing quantities of the second constituent, $C_6H_5CON(C_2H_5)_2$, were added, and the freezing points of their solutions (t_1) were determined. The difference ($t_0 - t_1$) = Δt indicated the change of the depression of the freezing point with concentration due to the addition of the second constituent. We used these figures to plot the composition – property diagram. The molar per cent of diethylbenzamide (Table 6, Column 4) was laid off on the axis of abscissas, with the values of Δt, i.e., the change in the depression of the freezing point with concentration laid off on the axis of ordinates. The results of cryoscopic measurements of the ICl – $C_6H_5CON(C_2H_5)_2$ – C_6H_5NO system are given in Table 6 and Fig. 5.

In this and the succeeding tables, n denotes deithylbenzamide (or acetanilide in Tables 11 and 12.)

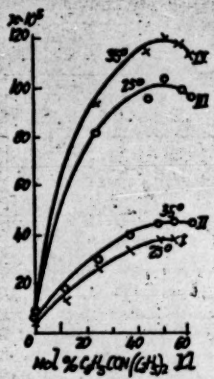

Fig. 4. Specific conductance of the ICl – $C_6H_5CON(C_2H_5)_2$ – $C_6H_5NO_2$ system.

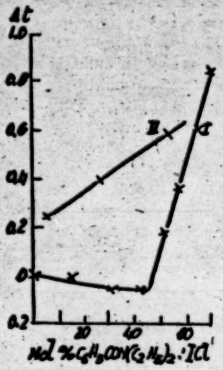

Fig. 5. Cryoscopy of the ICl – $C_6H_5CON(C_2H_5)_2$ system in nitrobenzene

TABLE 6

Cryoscopic Investigation of the ICl – $C_6H_5CON(C_2H_5)_2$ System in Nitrobenzene

$C_6H_5NO_2$, grams	ICl, grams	$C_6H_5CON(C_2H_5)_2$ grams	$C_6H_5CON(C_2H_5)_2$ / ICl + n in mol. %	t_0	t_1	Δt
21.4700	0.4039	–	0.00	3.775	–	0.000
21.4700	0.4039	0.0778	15.01	3.775	3.778	-0.003
21.4700	0.4039	0.1986	31.10	3.775	3.850	-0.007
21.4700	0.4039	0.3223	42.30	3.775	3.833	-0.058
21.4700	0.4039	0.4643	51.37	3.775	3.590	+0.185
21.4700	0.4039	0.5848	57.33	3.775	3.410	+0.365
21.4700	0.4039	0.8216	65.16	3.775	3.160	+0.615
21.4700	0.4039	1.0183	69.87	3.775	2.915	+0.860
21.4700	0.4039	1.6454	78.94	3.775	2.165	+1.610

The figures in column 7 of Table 6 indicate that as more diethylbenzamide is added to the nitrobenzol solution of ICl, the depression of the freezing point diminishes somewhat; only at the equimolecular proportion of $C_6H_5CON(C_2H_5)_2$ to ICl is there a sharp increase in the depression owing to an increase in the number of particles in the solution, due to the excess diethylbenzamide (Curve I, Fig. 5).

We also measured the freezing points of nitrobenzene solutions of diethylamine in order to compare them with the results of our cryoscopic measurements of the ternary system ICl – $C_6H_5CON(C_2H_5)_2$ – $C_6H_5NO_2$, and from these data we computed the molecular weight and the degree of association of the ethylbenzamide in the nitrobenzene. The results of these measurements are listed in Table 7 and are plotted in Fig. 5 (Curve II).

The data in Table 7 show that the diethylbenzamide is in a monomolecular state in extremely dilute solutions; as its concentration in the nitrobenzene is increased the diethylbenzamide molecules begin to associate, this process growing as the solution concentration is increased. We made a cryoscopic study of the $C_6H_5CON(C_2H_5)_2$ – ICl – $C_6H_5NO_2$ system in order to determine the molecular state of the coordination compound $C_6H_5CON(C_2H_5)_2 \cdot ICl$ dissolved in nitrobenzene. A known amount of the previously prepared coordination compound $C_6H_5CON(C_2H_5)_2 \cdot ICl$, secured by mixing exactly equivalent quantities of the two components, was added to a weighed quantity of nitrobenzene, and the freezing points of these solutions were measured. The results are listed in Table 8.

TABLE 7

Cryoscopic Investigation of $C_6H_5CON(C_2H_5)_2$ in Nitrobenzene

$C_6H_5NO_2$ (grams)	$C_6H_5CON(C_2H_5)_2$ (grams)	Δt	Molecular weight*	Degree of association
21.2257	0.2087	0.340	202.0	1.14
21.2257	0.5059	0.785	212.4	1.20
21.2257	0.8946	1.318	223.7	1.26
21.2257	1.1776	1.707	227.2	1.29

We see from the Figures in Table 8 that the molecular weight of the coordination compound $C_6H_5CON(C_2H_5)_2 \cdot ICl$ rises as the concentration of the latter in the solution increases.

TABLE 8

Cryoscopic Investigation of $C_6H_5CON(C_2H_5)_2 \cdot ICl$ in Nitrobenzene

$C_6H_5NO_2$, grams	$C_6H_5CON(C_2H_5)_2 \cdot ICl$ (grams)	mol.% of the coordination compound	Δt	Molecular weight**
24.8472	1.2901	1.84	1.132	231.1
24.8472	1.8942	2.68	1.583	337.1
24.8472	2.6246	3.68	2.107	350.9

According to our measurements, dilute nitrobenzene solutions of $C_6H_5CON(C_2H_5)_2 \cdot ICl$ are rather poor conductors of current, however. When this fact is compared with the data in Table 8 it may be concluded that in highly dilute solutions this coordination compound consists principally of monomeric molecules, somewhat dissociated into ions; the percentage of associated molecules rises considerably in more concentrated solutions. This may be the reason for the decrease in the depression (Δt) observed when the concentration of the coordination compound is increased (Fig. 5). In order to determine the nature of the ions into which the coordination compound $C_6H_5CON(C_2H_5)_2 \cdot ICl$ is dissociated we ran several tests to investigate the transfer of ions in the $C_6H_5CON(C_2H_5)_2 \cdot ICl$ – $C_6H_5NO_2$ system. Electrolysis was conducted in the container described by us in previous reports [1]. The electrodes were made of platinum. The electrolyte was prepared as follows: An exactly equimolecular quantity of $C_6H_5CON(C_2H_5)_2$ was added to a known quantity of iodine chloride in a small flask fitted with a ground-glass stopper, and then a certain quantity of nitrobenzene was poured in. The solution was shaken up, tightly sealed, and stored in a desiccator. An electrolyte containing 8.38 mol. % (or 20.1% by weight) of $C_6H_5CON(C_2H_5) \cdot ICl$ was used in all three tests. The first and second tests lasted 4 hours and 20 minutes and 6 hours, respectively, while the third test lasted 2 hours and 15 minutes. The current ranged from 4 to 10

* The theoretical molecular weight of $C_6H_5CON(C_2H_5)_2$ is 177.0.

** The theoretical molecular weight of $C_6H_5CON(C_2H_5)_2 \cdot ICl$ is 339.38.

TABLE 9

Test No.	Copper deposited in the coulometer (g)		Grams of chlorine and iodine in the electrolyte				Difference		I:Cl ratio after electrolysis	Grams that should be evolved according to the coulometer reading	
			Before electrolysis		After electrolysis		Cl	I		Cl	I
			Cl	I	Cl	I					
1	2		3	4	5	6	7	8	9	10	11
1	0.0377	anolyte	0.1688	0.6041	0.2552	0.7615	+0.0864	+0.1574	0.83	0.0421	0.1505
		catholyte	0.1720	0.6158	0.0823	0.4632	-0.0897	-0.1527	1.57		
2	0.0528	anolyte	0.1684	0.6028	0.2645	0.8503	+0.0961	+0.2475	0.89	0.0590	0.2108
		catholyte	0.1713	0.6131	0.0750	0.3808	-0.0997	-0.2323	1.41		
3	0.0087	anolyte	0.1573	0.5796	0.1678	0.5838	+0.0105	+0.0042	0.97	0.0097	0.0347
		catholyte	0.1468	0.5614	0.1292	0.5584	-0.0166	-0.0030	1.20		

milliamperes. The results of these tests are given in Table 9

The data in Table 9 show that, as in the systems we had investigated previously: acetamide (or benzamide – iodine chloride, the iodine:chlorine ratio in the electrolyte after analysis rose in the catholyte (>1) and dropped in the anolyte (<1), the absolute content of iodine and chlorine diminishing in the catholyte and increasing in the anolyte. The iodine transferred to the catholyte as a cation and discharged at the cathode then begins to migrate to the anolyte, as has been observed in the electrolysis of nitrobenzene solutions of iodine [7]. This explains the absolute increase in the amount of iodine in the anolyte. The electrolytic processes in these systems may be represented as follows:

$$[R\cdot I]Cl \rightleftarrows [RI]^+ + Cl^- \quad (I),$$

for the monomeric molecules $(R\cdot IX)_1$ and

$$[R_2\cdot I][ICl_2] \rightleftarrows [R_2\cdot I]^+ + [ICl_2]^- \quad (II)$$

for the dimeric molecules $(R\cdot IX)_2$.

In dilute solutions, where the coordination compound $C_6H_5CON(C_2H_5)_2\cdot ICl$ is in the monomeric state, dissociation takes place in accordance with Equation (I). In more concentrated solutions where much of the coordination compound is in the associated state, the dissociation of the dimeric molecules predominates – Equation (II).

The results of our cryoscopic tests (Table 8) show that $C_6H_5CON(C_2H_5)_2\cdot ICl$ solutions contain a fairly large number of associated molecules even at 3.6 mol.%, the degree of association being still higher, of course at a concentration of 8.38 mol.% (as in our electrolysis experiments). The latter circumstance explains the fact that the amount of chlorine and iodine transferred from the catholyte to the anolyte during the passage of 1 F is very close to one gram-ion of ICl_3^-, i.e., one gram-atom of iodine is transferred together with two gram atoms of chlorine. When we compare, for example, the theoretical quantities of I + Cl that should have been transferred according to the coulometer readings (Columns 10 and 11 in Table 9) with the actual aggregate quantities of iodine and chlorine that were transferred (Columns 7 and 8) for Experiments 1 and 2 in that table,

[3] When the electrolysis is prolonged the catholyte acquires the peculiar odor of diethylbenzamide, while anolyte smells of chlorine.

get the following tabulation (Table 10):

TABLE 10

Test No.	Theoretical quantity of I+2Cl, grams	Iodine and chlorine actually transferred (grams)
1	0.2347	0.2438
2	0.3288	0.3436

The results of Experiment 3 can be used only qualitatively, owing to the short duration of the experiment.

The results of the experiment described above enable us to reach the following conclusions: a) diethylbenzamide forms a coordination compound, $C_6H_5CON(C_2H_5)_2 \cdot ICl$, with iodine chloride; b) the physicochemical properties of this coordination compound: its conductance, the kind of ions, and its behavior during electrolysis,- are the same as those of the analogous coordination compound formed by unsubstituted benzamide, $C_6H_5CONH_2 \cdot ICl$ [3]. However, diethylbenzamide cannot undergo a tautomeric change and reacts with the iodine chloride only in its amide form. We may therefore conclude that the coordination compound of ICl with unsubstituted benzamide is also a product of the addition of ICl to the amide form of benzamide.

3. $ICl - C_6H_5NHCOCH_3$ System

We have measured the specific conductance of the $ICl - C_6H_5NHCOCH_3 - C_6H_5NO_2$ system and investigated it cryoscopically. The specific conductance of this system is given in Table 11 and Fig. 6.

TABLE 11

Specific Conductance of the System $ICl - C_6H_5NHCOCH_3 - C_6H_5NO_2$ *

$C_6H_5NHCOCH_3$ / ICl + n (mol.%)	Specific conductance, $\kappa \cdot 10^4$	
	25°	35°
0.00	1.97	2.33
17.27	31.12	35.82
24.30	36.54	41.21
36.36	39.55	44.65
44.40	37.14	42.73
48.69	34.51	38.02
53.05	32.47	36.28
67.97	22.30	-
72.08	20.45	26.44

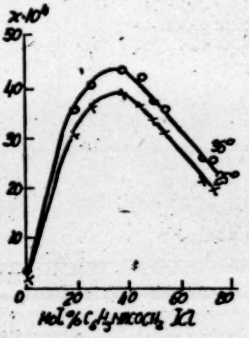

Fig. 6. Specific conductance of the $ICl - C_6H_5NHCOCH_3 - C_6H_5NO_2$ system.

The specific conductance of this system rises as more acetanilide is added up to the point where the latter represents 33.3 mol.% of the ICl. Any further addition of the anilide produces a drop in the conductance.

The $ICl - C_6H_5NHCOCH_3 - C_6H_5NO_2$ system was investigated cryoscopically like the systems containing diethylbenzamide.

The results of our measurements are given in Table 12 and Fig. 7; we see that as acetanilide is added, not only does the depression not increase, but, on the contrary, it diminishes until the $C_6H_5NHCOCH_3$:ICl ratio approximates 1:2. Thereafter, the curve representing the variation of the depression with temperature rises sharply, vaying nearly linearly with the concentration of acetanilide.

* Mole of ICl/mole of $C_6H_5NO_2$ = 1/10.49.

TABLE 12

Cryoscopic Investigation of the ICl – $C_6H_5NHCOCH_3$ System In Nitrobenzene

$C_6H_5NO_2$ (grams)	ICl (grams)	$C_6H_5NHCOCH_3$ (grams)	$C_6H_5NHCOCH_3$ / ICl + n (mol. %)	Freezing point t_0	Freezing point t_1	Δ t
21.7681	0.5375	–	0.00	3.615	3.615	0.000
21.7681	0.5375	0.0351	7.15	3.615	3.845	-0.230
21.7681	0.5375	0.1475	24.84	3.615	3.985	-0.370
21.7681	0.5375	0.2015	31.07	3.615	4.030	-0.415
21.7681	0.5375	0.2695	37.60	3.615	3.990	-0.375
21.7681	0.5375	0.3322	42.64	3.615	3.960	-0.345
21.7681	0.5375	0.3764	45.72	3.615	3.905	-0.290
21.7681	0.5375	0.4308	49.08	3.615	3.810	-0.195
21.7681	0.5375	0.5058	53.09	3.615	3.770	-0.155
21.7681	0.5375	0.6144	57.89	3.615	3.625	-0.110
21.7681	0.5375	0.8191	64.70	3.615	3.365	+0.250
21.7681	0.5375	1.0583	70.31	3.615	3.135	+0.480

The results of all these tests justify the conclusion that acetanilide and iodine chloride unite in a nitrobenzene solution to form the coordination compound $C_6H_5NHCOCH_3 \cdot 2ICl$, with apparently this structure: $[C_6H_5NHCOCH_3 \cdot I][ICl_2]$. We computed the molecular weight of the coordination compound $C_6H_5NHCOCH_3 \cdot 2ICl$ in a nitrobenzene solution from our cryoscopic measurements (the mean values of Tests 4 and 5 in Table 12) in which the $C_6H_5NHCOCH_3$ to ICl ratio was close to 1:2; it was found to be 406.3. This molecular weight is smaller than the value derived from the formula, which is 459.8. This is in conformity with the circumstance that nitrobenzene solutions of the ICl – $C_6H_5NHCOCH_3$ system are conductors, the specific conductance of such solutions being of the order of 10^{-3} $ohm^{-1}cm^{-1}$.

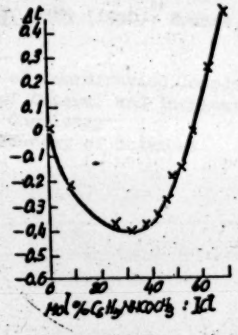

Fig. 7. Cryoscopy of the ICl – $C_6H_5NHCOCH_3$ system in nitrobenzene.

The conductance and the shape of the conductance isotherms of the ICl – $C_6H_5NHCOCH_3$ – $C_6H_5NO_2$ system are very much like those of the analogous systems containing acetamide, benzamide, or diethylbenzamide.

SUMMARY

1. The diethylbenzamide – iodine chloride system has been investigated by the viscosity, conductance, and cryoscopy methods. It has been proved that a compound with the composition of $C_6H_5CON(C_2H_5)_2 \cdot ICl$ is formed in this system, possessing the properties of a fairly strong electrolyte and dissociating in accordance with:

$$[C_6H_5CON(C_2H_5)_2 \cdot I]Cl \rightleftarrows [C_6H_5CON(C_2H_5)_2 \cdot I]^+ + Cl^-.$$

The following structure is suggested for the dimer molecules of this coordination compound on the basis of a study of ion transfer in nitrobenzene solutions:

$$\{[C_6H_5CON(C_2H_5)_2]\cdot I\}^+ [ICl_2]^- .$$

2. The conductance of the acetanilide – iodine chloride system has been measured and it has been investigated cryscopically. It has been found that the coordination compound $C_6H_5NHCOCH_3 \cdot 2ICl$, which is a good conductor, is formed.

3. The systems of iodine chloride with substituted acid amides and the coordination compounds formed in these systems are quite similar to the corresponding systems and coordination compounds, respectively, that consist of iodine chloride and the unsubstituted acid amides ($C_6H_5CONH_2$, CH_3CONH_2). It is therefore concluded that acid amides react with ICl in their amide form.

LITERATURE CITED

[1] Ya.A.Fialkov and I.D.Muzyka, J.Gen.Chem. 18, 802 (1948).

[2] Ya.A.Fialkov and I.D.Muzyka, J.Gen.Chem. 18, 1205 (1948).

[3] Ya.A.Fialkov and I.D.Muzyka, J.Gen.Chem. 19, 1416 (1949).*

[4] Ber., 9, 346 (1876).

[5] Ya.A.Fialkov, O.I.Shor, J.Gen.Chem. 18, 14 (1948).

[6] Ya.A.Fialkov and I.D.Muzyka, J.Gen.Chem. 20, 385 (1950);** Brunes, Galecki, Z. phys. Chem. 84, 513 (1913).

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*See CB translation p. 1417 ff.
**See CB translation p. 407 ff.

COMPOUNDS OF ALUMINUM HALIDES WITH DIOXANE

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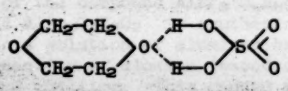
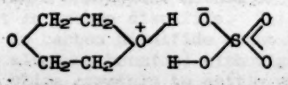
In the course of an investigation of the dielectric constants and polarization of the ternary system aluminum bromide – dioxane – benzene, we discovered two characteristic points on the composition – dielectric constant curve of the solution. The first point, which was the maximum deviation on the $\Delta\varepsilon$ – composition curve, represented the compound $AlBr_3 \cdot C_4H_8O_2$. The second point, which was a minimum on the $\Delta\varepsilon$ – composition curve, corresponded to the compound $Al_2Br_6 \cdot C_4H_8O_2$. Since up to now only the aluminum bromide–dioxane compound, $AlBr_3 \cdot 2C_4H_8O_2$, has been described [1], we were impelled to make a fuller study of the reaction of aluminum bromide with dioxane.

What is characteristic of dioxane is the comparative ease with which it forms coordination compounds, as is evidenced by the rather large number of such compounds already isolated. Favorsky [2], for instance, secured compounds of dioxane with bromine, iodine, and sulfuric and picric acids. Dioxane also constitutes molecular compounds with many metal halides. We know of coordination compounds of dioxane with halides of the alkali metals and ammonia and with halides of Group 2 metals (calcium, barium, magnesium, zinc, and mercury). Dioxanates of the trihalides of arsenic, antimony, and bismuth have been secured and their thermal stability determined [3]. At the present time some of the electrical properties of individual dioxanates have likewise been investigated. Syrkin and Anisomov [4], for example, have made a study of the polar properties of compounds of dioxane with sulfuric acid, bromine, and iodine. The dipole moment of the compound $C_4H_8O_2 \cdot H_2SO_4$ was found to be 4.63 D, which indicates, according to these authors, that hydrogen bonds (I) as well as oxonium structures (II) are produced in these compounds:

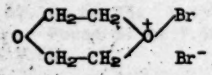


(I)



(II)

Compounds of dioxane with bromine or iodine possess smaller dipole moments than those with sulfuric acid; calculation indicates, however, that oxonium structures play a certain role in these compounds too:



The present paper deals with coordination compounds of aluminum bromide and chloride with dioxane and with the determination of the dipole moments of these compounds.

EXPERIMENTAL

The aluminum bromide and chloride used in this research were prepared in the usual manner. Chemically pure dioxane was kept for two weeks above metallic sodium (to remove any traces of moisture) and was distilled over the same metal. The boiling point of the dioxane was 101.0-101.3° at 750 mm, while its specific gravity was 1.0329 at 20°. All the reagents were stored in sealed ampoules.

I. Coordination Compounds of Aluminum Bromide and Dioxane

The compound $AlBr_3 \cdot 2C_4H_8O_2$. The compound $AlBr_3 \cdot 2C_4H_8O_2$ was prepared by placing a solution of aluminum bromide in dioxane, saturated at 45-50°, in a glass test tube, which was drawn out in its middle section, and then sealing the test tube. As the solution was gradually cooled, elongated, thin, colorless, transparent crystals settled out. When the crystallization process was complete, the test tube was reversed, and the mother liquid was decanted into the other end of the test tube, thus separating it from the crystals. The lower end of the test tube, containing the mother liquor, was immersed in a freezing mixture, while the upper end, containing the crystals, was warmed with hot air (50-60°). After three days had elapsed, with the crystals completely separated from the mother liquor and wholly dry, the test tube was sealed off in the center. This procedure made it possible to secure well-faced crystals up to 10 mm long, while keeping atmospheric moisture out. The crystals are prisms with rhombic syngony. They were analyzed for their bromine content (by the Volhard method) and for aluminum (as Al_2O_3). The results of analysis were as follows:

0.8906 g, 0.5582 g, 1.9726 g substance: 0.4750 g, 0.2998 g, 1.0510 g Br. Found %: Br 53.34, 53.69, 53.28; 0.5582 g, 0.8906 g, 1.9726 g substance: 0.0650 g, 0.1010 g, 0.2214 g Al_2O_3. Found %: Al 6.16, 6.00, 5.94. $AlBr_3 \cdot 2C_4H_8O_2$. Computed %: Br 54.13; Al 6.09.

The synthesized compound is the same as the compound previously described by Mezhenny [1]. The coordination compound $AlBr_3 \cdot 2C_4H_8O_2$ fuses with decomposition in the 70-80° range and is decomposed by water; its solubility in benzene is about 11% at 20°.

The compound $AlBr_3 \cdot C_4H_8O_2$. The coordination compound $AlBr_3 \cdot C_4H_8O_2$ can be prepared from the compound $AlBr_3 \cdot 2C_4H_8O_2$ by splitting off one molecule of the dioxane. When the transparent crystals of $AlBr_3 \cdot 2C_4H_8O_2$ are heated over a water bath to 100° in a vacuum set up by a water-jet pump, they rapidly grow dim, turn white, and disintegrate. Analysis proves that this results in the production of the compound $AlBr_3 \cdot C_4H_8O_2$. A more convenient method of preparing the compound $AlBr_3C_4H_8O_2$ is synthesizing it in carbon disulfide. This was done by adding to a solution of aluminum bromide in carbon disulfide about three times the quantity of dioxane (based on the aluminum bromide) with vigorous agitation and chilling. This caused minute white crystals to settle out of the solution. After separation from the mother liquor the crystals were dried for a short time in vacuum, at a pressure of 15-25 mm Hg. No changes were observed in the synthesized compound during this drying. Analysis indicated that the compound has the composition of $AlBr_3 \cdot C_4H_8O_2$.

1.4944 g, 1.3398 g, 1.3244 g substance: 1.0050 g, 0.8990 g, 0.8838 g Br. Found %: Br 67.25, 67.10, 66.73. 1.3348 g, 1.3244 g substance: 0.1846 g, 0.1850 g, Al_2O_3. Found %: Al 7.32, 7.39. $AlBr_3 \cdot C_4H_8O_2$. Computed %: Br 67.57; Al 7.60.

The melting point of the coordination compound $AlBr_3 \cdot C_4H_8O_2$ was 114.5° in a sealed capillary; its solubility in benzene at 20° was about 7%.

The coordination compound $Al_2Br_6 \cdot C_4H_8O_2$. The coordination compound

$Al_2Br_6 \cdot C_4H_8O_2$ was synthesized by gradually adding enough dioxane, with chilling, to a solution of aluminum bromide in benzene to leave an excess of aluminum bromide over the quantity called for by the formula. The finely crystalline white precipitate was repeatedly washed with anhydrous benzene until all the unreacted aluminum bromide was eliminated and then dried in vacuum.

Analysis of the resulting compound yielded the following results.

2.0384 g substance: 1.5656 g Br. 0.9660 g substance: 0.1580 g Al_2O_3. Found %: Br 76.80; Al 8.65. $Al_2Br_6 \cdot C_4H_8O_2$. Computed %: Br 77.10; Al 8.67.

The compound $Al_2Br_6 \cdot C_4H_8O_2$ remains unchanged when heated in a sealed capillary to 190°; it darkens as the temperature is raised still higher, and at 237-240° it fuses with decomposition and the evolution of considerable hydrogen bromide. The solubility of the coordination compound $Al_2Br_6 \cdot C_4H_8O_2$ in benzene is about 1% at 20°. Solutions of the coordination compounds of aluminum bromide and chloride with dioxane in benzene are nonconductors. Aluminum bromide in dioxane is likewise practically a nonconductor, the specific conductance of a saturated solution (about 20%) of aluminum bromide in dioxane at 25° being $5 \cdot 10^{-8}$ mhos.

The results of cryoscopic investigations of the dioxanates of aluminum bromide and chloride in benzene are given in Table 1. The stability of the synthesized compounds may be judged by comparing these figures with the properties of the dioxanates of aluminum halides cited above.

TABLE 1

Molecular Weight of Coordination Compounds of Aluminum Bromide and Chloride with Dioxane in Benzene; $K_{benzene} = 5.12$

Compound	%	Δ t	M	
			Found	Calc
$AlBr_3 \cdot C_4H_8O_2$	0.80	0.115	361	
	2.25	0.333	354	354.8
	3.83	0.590	345	
$AlBr_3 \cdot 2C_4H_8O_2$	0.75	0.160	242	
	1.68	0.385	227	442.9
	4.51	1.025	235	
$Al_2Br_6 \cdot C_4H_8O_2$	0.63	0.053	616	621.5
$AlCl_3 \cdot 2C_4H_8O_2$	0.41	0.120	177	309.5
	0.57	0.172	171	

1. $AlBr_3 \cdot C_4H_8O_2$ is a stable compound: it fuses without decomposition, and its cryoscopic data indicate that it is stable in benzene solutions, existing in the monomolecular state and not decomposing.

2. The compound $AlBr_3 \cdot 2C_4H_8O_2$ is unstable, fusing with decomposition. When the coordination compound is heated to 70-80°, the dioxane is partially driven off. When crystals of the compound $AlBr_3 \cdot 2C_4H_8O_2$ are kept under a vacuum of 15-20 mm Hg, they gradually lose one molecule of dioxane, tarnish, turn white, and are converted into the coordination compound $AlBr_3 \cdot C_4H_8O_2$. The cryoscopic determinations likewise indicate that the observed molecular weight of the coordination compound $AlBr_3 \cdot 2C_4H_8O_2$ is about half that of the calculated value. Since benzene solutions of aluminum dioxanates are nonconductors, this decrease in the molecular weight cannot be attributed to electrolytic dissociation, so that the experimental molecular weight proves that the compound $AlBr_3 \cdot 2C_4H_8O_2$ is unstable, being decomposed in benzene into two molecules ($AlBr_3 \cdot C_4H_8O_2$ and $C_4H_8O_2$). These data are evidence that the second molecule of dioxane in the coordination compound $AlBr_3 \cdot 2C_4H_8O_2$ is less firmly attached to the aluminum bromide than the first one. A similar state of affairs exists in the $AlCl_3 \cdot 2C_4H_8O_2$ dioxanate of aluminum chloride.

3. When $Al_2Br_6 \cdot C_4H_8O_2$ is heated to 190°, it does not change perceptibly; only at 237-240° does it fuse with decomposition and evolution of large quantities of hydrogen bromide. The high m.p., considerably exceeding that of dioxane and aluminum bromide, together with the normal molecular weight (cryoscopic, in benzene - Table 1), indicate that the compound $Al_2Br_6 \cdot C_4H_8O_2$ is stable.

The compound $AlCl_3 \cdot 2C_4H_8O_2$. We prepared the coordination compound $AlCl_3 \cdot 2C_4H_8O_2$ by the same method as the corresponding compound of dioxane with aluminum bromide. Large, transparent, colorless crystals, up to 20 mm long, settled out of a dioxane solution of aluminum chloride when it cooled after it had been heated to 40-50°. The results of analysis are given below.

0.8046 g, 0.3174 g, 1.8146 g substance: 0.2752 g, 0.1078 g, 0.6218 g Cl. Found %: Cl 34.21, 33.96, 34.27. 1.8146 g substance: 0.2978 g Al_2O_3. Found %: Al 8.68. $AlCl_3 \cdot 2C_4H_8O_2$. Computed %: Cl 34.36; Al 8.71.

The crystals have the form of rhombic prisms (rhombic syngony). The compound $AlCl_3 \cdot 2C_4H_8O_2$ is stable when heated to 106°; above that temperature part of the dioxane is driven off, the compound fusing completely at 114°. The one molecule of dioxane may also be split off from the $AlCl_3 \cdot 2C_4H_8O_2$ at a lower temperature in vacuum. The transparent crystals then tarnish, turn white, and disintegrate, the white powder of $AlCl_3 \cdot C_4H_8O_2$ being formed.

The compound $AlCl_3 \cdot C_4H_8O_2$. The compound $AlCl_3 \cdot C_4H_8O_2$ can be prepared from nitromethane solutions. This was done by gradually adding dioxane to aluminum chloride dissolved in nitromethane. The finely crystalline white precipitate was separated from the mother liquor, washed 2-3 times with nitromethane, then several times with benzene, and dried in vacuum.

1.0746 g, 1.1694 g substance: 0.5172 g, 0.5602 g Cl. Found %: Cl 48.14, 47.91. 1.3094 g, 1.0746 g substance: 0.3030 g, 0.2470 g Al_2O_3. Found %: Al 12.24, 12.16. $AlCl_3 \cdot C_4H_8O_2$. Computed %: Cl 48.03; Al 12.18.

The compound $AlCl_3 \cdot C_4H_8O_2$ fused without perceptible changes. The melting point in a sealed capillary was 154.5-155°.

III. Dipole Moments of the Dioxanates of Aluminum Bromide and Chloride

The dipole moments of the coordination compounds of the aluminum halides with dioxane were measured in benzene solutions. The dielectric constants were measured by the beat method at the wavelength of 301.3 meters at 20 and 25°. The total polarization $P_{2\infty}$ was calculated by extrapolation to infinite dilution.

The electron polarization was computed from the sum of the refraction of the aluminum bromide or chloride, determined in dioxane, and the refraction of pure dioxane. The molar refraction, determined at 20° with the D-line of sodium, was 29.0 cm^3 for aluminum bromide and 21.5 cm^3 for aluminum chloride. The atom polarization was assumed to be 10% of the molar refraction. The dioxanates of the aluminum halides were prepared by the method described above. Table 2 gives the results of our determinations of the dielectric constants and of the specific gravities, as well as the polarization values computed therefrom. The dipole moments

TABLE 2

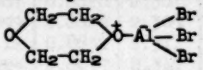
Dielectric Constants and Polarization of the Dioxanates of Aluminum Bromide and Chloride in Benzene at 25°

Compound	C_2	d	ε	P_2
$AlBr_3 \cdot C_4H_8O_2$	0	0.8742	2.271	–
	0.002950	0.8809	2.388	620
	0.004508	0.8845	2.453	622
	0.005517	0.8868	2.495	620
	0.006905	0.8900	2.553	617
	0.007433	0.8912	2.575	615
	P_∞ = 625 cm^3			
$AlCl_3 \cdot C_4H_8O_2$	0.000414	0.8749	2.287	607
	0.001075	0.8760	2.314	606
	0.001562	0.8769	2.334	607
	0.002197	0.8780	2.360	605
	P_∞ = 607 cm^3			

were calculated from the equation

$$\mu = 0.0127 \sqrt{P_0 T} \cdot 10^{-18} \text{ e.s.u.}$$

The results are tabulated in Table 5. The dipole moment of the compound $AlBr_3 \cdot C_4H_8O_2$ is 5.23 D, and that of the corresponding compound with aluminum chloride, $AlCl_3 \cdot C_4H_8O_2$, is 5.19 D. When it is borne in mind that the dipole moments of dioxane and of aluminum bromide are zero [5], these large dipole moments must be attributed to the formation of a bond between the aluminum halide and the dioxane. The size of the moment of the bond in coordination compounds of aluminum halides with dioxane approximates or equals that of the corresponding moments in compounds of aluminum halides with ethyl ether, diphenyl ether, anisole, etc. [6]. The oxygen in the dioxane largely tends to produce oxonium type compounds (tervalent positive oxygen), while the aluminum in the aluminum bromide is a good acceptor of electrons. Hence, the reaction of aluminum bromide with dioxane ought to involve the formation of a new coordinate bond. And, in fact, the large dipole moment of the compound $AlBr_3 \cdot C_4H_8O_2$ confirms the existence of such a bond. Moreover, the large dipole moments of the dioxanates of aluminum bromide and chloride indicate that the coordinate bond formed in the complex molecule is highly polarized, as may be shown diagrammatically by the subjoined formula.



Determination of the dipole moments of coordination compounds of aluminum bromide and chloride containing two molecules of dioxane (Table 3) demonstrated that they were 5.19 D for $AlBr_3 \cdot 2C_4H_8O_2$ and 5.21 D for $AlCl_3 \cdot 2C_4H_8O_2$ (Table 5), that is, they fully agree with the magnitudes of the dipole moments for $AlBr_3 \cdot C_4H_8O_2$ and $AlCl_3 \cdot C_4H_8O_2$. This identity of the dipole moments may be readily explained by the fact that the dioxanates of the aluminum halides, $AlBr_3 \cdot 2C_4H_8O_2$ and $AlCl_3 \cdot 2C_4H_8O_2$, are decomposed in benzene solutions, splitting off one molecule of dioxane, the dipole moments of the compounds $AlBr_3 \cdot C_4H_8O_2$ and $AlCl_3 \cdot C_4H_8O_2$ being determined in the solutions in both cases. The unstable addition of the second molecule of dioxane in the compounds $AlBr_3 \cdot 2C_4H_8O_2$ and $AlCl_3 \cdot 2C_4H_8O_2$ is apparently due to the fact that these compounds are formed as the result of the inductive interaction of the highly polar molecules $AlHal_3 \cdot C_4H_8O_2$ with the nonpolar molecules of dioxane. Further research is necessary to confirm these conclusions and to determine the nature of the bond in compounds of the aluminum halides with dioxane that contain various amounts of dioxane. We were also interested in ascertaining the structure of the coordination compound $AlBr_3 \cdot C_4H_8O_2$. Physicochemical investigation has shown that the compound $Al_2Br_6 \cdot C_4H_8O_2$ is fairly stable, existing as undissociated monomeric molecules in benzene solutions. It might be assumed that both of the oxygen atoms in the dioxane take part in the formation of this coordination compound. If both of the dioxane oxygen atoms acted alike in the formation of the compound $Al_2Br_6 \cdot C_4H_8O_2$, the latter's

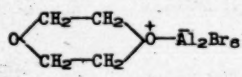
TABLE 3

Dielectric Constants and Polarization of the Compounds $AlX_3 \cdot 2C_4H_8O_2$ in Benzene at 25°

Compound	C_2	d	ε	P_2
$AlBr_3 \cdot 2C_4H_8O_2$	0	0.8742	2.271	–
	0.007354	0.8913	2.553	617
	0.009792	0.8970	2.650	611
	0.011725	0.9015	2.726	605
	0.014581	0.9082	2.838	596
	0.016856	0.9135	2.927	589
	0.019606	0.9199	3.032	579
	$P_{2\infty}$ = 640			
$AlCl_3 \cdot 2C_4H_8O_2$	0.000996	0.8749	2.307	612
	0.002588	0.8760	2.359	576
	$P_{2\infty}$ = 635			

pole moment ought to be zero, inasmuch as the moments of the $\bar{Al}—\overset{+}{O}$ bonds would then cancel each other out. Actually, however, our determination of the dipole moment of the compound $Al_2Br_6 \cdot C_4H_8O_2$ in benzene (Table 4) indicates that its dipole moment is 4.62 D (Table 5), so that the moments of the $\bar{Al}—\overset{+}{O}$ bonds do not cancel each other out.

We may therefore conclude that only one of the dioxane oxygen atoms takes part in the formation of the coordination compound $Al_2Br_6 \cdot C_4H_8O_2$, forming a single coordinate bond with the double molecule of aluminum bromide, which is manifested in the large dipole moment. The large dipole moment may also indicate that the compound $AlBr_3 \cdot C_4H_8O_2$ is largely polarized:



Here the double molecule of aluminum bromide carries a negative charge. In conclusion, we wish to point out that the formation of dioxanates of aluminum halides of different composition is an interesting peculiarity of dioxane as a constituent of coordination compounds. This peculiarity is closely related, apparently, to the fact that dioxane exhibits a greater tendency than the ethers to form compounds of the oxonium type.

TABLE 4

Dielectric Constants and Polarization of the Compound $Al_2Br_6 \cdot C_4H_8O_2$ in Benzene, at 25°

C_2	d	ε	P_2
0	0.8785	2.283	
0.00039	0.8795	2.294	546
0.00049	0.8800	2.296	505
0.00065	0.8809	2.301	502
0.00087	0.8820	2.307	490
0.00099	0.8826	2.308	452
0.00111	0.8832	2.311	450
0.00124	0.8837	2.315	457

$P_\infty = 540$

TABLE 5

Compound	P_∞	$P_E + P_A$	P_O	$\mu \cdot 10^{18}$ e.s.u.
$AlBr_3 \cdot C_4H_8O_2$	625	55	570	5.23
$AlBr_3 \cdot 2C_4H_8O_2$	640	80	560	5.19
$Al_2Br_6 \cdot C_4H_8O_2$	540	88	452	4.62
$AlCl_3 \cdot C_4H_8O_2$	607	47	560	5.19
$AlCl_3 \cdot 2C_4H_8O_2$	635	70	565	5.21

SUMMARY

1. The following coordination compounds of aluminum bromide and chloride with dioxane have been synthesized: $AlBr_3 \cdot C_4H_8O_2$, $Al_2Br_6 \cdot C_4H_8O_2$, $AlCl_3 \cdot C_4H_8O_2$, and $AlCl_3 \cdot 2C_4H_8O_2$.

2. The dipole moments of the coordination compounds of aluminum bromide and chloride with dioxane have been determined, and the most probable structures have been proposed for these compounds.

LITERATURE CITED

[1] Ya.F.Mezhenny, J.Gen.Chem. 16, 447 (1946).

[2] A.E.Favorsky, J.Russ.Phys.Chem.Soc. 38, 747 (1906).

[3] H.Reinbold, A.Luyken, H Schmittmann, J. prak. Chem. 148, 81 (1937); 149, 30 (1937); C. Kelley and P. McCusker, J.Am.Chem.Soc., 65, 1307 (1943).

[4] Ya.K.Syrkin and K.M.Anisimov, Proc.Acad.Sci. USSR 54, 1457 (1948).

[5] V.A.Plotnikov, I.A.Sheka, and Z.A.Yankelevich, J.Gen.Chem. 9, 868 (1939); C.P.Smythe: Dielectric Constant and Molecular Structure (Russ. ed), 256 (1937).

[6] I.A.Sheka, J. Phys. Chem. 14, 340 (1940); 16, 99 (1942).

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REACTIONS OF ALIPHATIC DIAZO COMPOUNDS WITH UNSATURATED COMPOUNDS

VII. THE REACTION OF ETHYL DIAZOACETATE WITH VINYL ETHYL ETHER

I. A. Dyakonov and N. A. Lugovtsova

Rambaud [1] was the first to synthesize the ethyl ester of 2-ethoxycyclopropane-1-carboxylic acid, in 1938, by reacting sodium ethylate with esters of γ-chloro- or γ-bromocrotonic acids, the yields being 3 and 18% of the theoretical, respectively. As has been pointed out earlier, in the course of our researches in an adjacent field [2-6], the necessity soon arose of checking Rambaud's data on the properties of 2-ethoxycyclopropane-1-carboxylic acid, (II) and its ethyl ester (I). This goal has been partially achieved in the present report. In contrast to the method employed by Rambaud, we synthesized [illegible] the ester (I) by means of the following reaction:

$$C_2H_5O{-}CH{=}CH_2 + N_2CH{-}COOC_2H_5 \xrightarrow[Cu]{CuSO_4} C_2H_5O{-}\overset{\diagup\ \diagdown}{CH}{-}\underset{\diagdown\ \diagup}{CH}{-}COOC_2H_5 + N_2 \qquad (1)$$

CH_2

already tested for other products [2,3].

When we use purified ethyl diazoacetate (distilled with steam in vacuum) and a $CuSO_4$ catalyst, the yield of the crude ester is 70% of the theoretical (cf I, A in the experimental section). The crude ester contains a trace (2.5-3%) of an ester of fumaric acid [7], which can be eliminated by treating the cold solution with potassium permanganate. The yield of the pure cyclic ester (I) was 60-63% of the theoretical, based on the ethyl diazoacetate originally used in the synthesis. When crude ethyl diazoacetate is used in the reaction, the conditions otherwise remaining the same, the reaction is less uniform, and the yield of the cyclic ester is lower (43.4% of the theoretical), owing to the formation of a larger quantity of ethyl fumarate. When Natur Cupfer C is used as a catalyst, no reaction takes place at all unless the reaction mixture is diluted with an inert solvent that has a higher boiling point than vinyl ethyl ether, such as ligroin. Dilution with ligroin, however, results in a progressive increase in the percentage of the ethyl fumarate in the reaction product (cf I, C). Increasing the amount of the vinyl ether in the ligroin-ether mixture, on the other hand, reduces the rate at which the ethyl diazoacetate decomposes while improving the yield of the cyclic ester (I). The optimum yield of the ester (I) (40-48% of the theoretical) in an experiment that did not last too long (8-9 hours) was achieved with $CuSO_4$ as the catalyst and ligroin as the diluent, the volumes of ligroin and vinyl ether used for the reaction being approximately 1:1 (cf I, D). The constants of the pure cyclic ester (I) produced by either method (the boiling point and the specific gravity) were close to those cited by Rambaud [1]. As was the case with Rambaud, the molar refraction equivalent proved to be somewhat higher than the value expected for a compound with a trimethylene ring. Both Rambaud and we observed an increase in the increment for the trimethylene ring when measuring the refraction of 2-ethoxycyclopropane-

arboxylic acid (II), produced by hydrolyzing the ester (I) (vide infra). We had secured analogous results earlier in our investigation of 2-butoxycyclopropanecarboxylic acid [4] and its ester [2]. We found that the ring increment I_D = = 1.07 - 1.08 for both acids and their esters, as against the value of 0.66 - 0.7 given in the literature. It may be that the discrepancy in the cases described above is due to the influence of the alkoxy and carboxyl groups on the three-membered ring. The ester (I) is not attacked by a cold solution of potassium permanganate, but when it is heated with such a solution, it is oxidized to succinic and acetic acids.

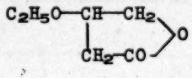
$$(I) \xrightarrow{KMnO_4} 2CH_3COOH + HOOC-CH_2-CH_2-COOH. \qquad (2)$$

Here too, the production of succinic acid as the result of oxidation may be considered as evidence of cyclic structure [2,3]. The cyclic structure of the ester was also borne out by measuring its Raman spectrum. We found 6 bright lines in the ester's spectrum with frequencies of (858)5; 1218(3); 1446(5); 2980(2); 3015(2), and 3069(1); as indicated in the literature [14-17], these lines are characteristic of a trimethylene ring. Moreover, we found two weaker lines in the ester's spectrum with frequencies that are also characteristic of the trimethylene ring: 751(0.5) and 1197(0.5) [14-16].* The frequency 1723(3) was found for the carbonyl group in the ester (I), in agreement with Rambaud's data [17], obtained in his measurements of the Raman spectra of the esters of cyclopropanecarboxylic acid.** The structure of the ester (I) was likewise established by hydrolysis in both an acid and an alkaline medium. As in the esters of butoxy- and acyloxycyclopropanecarboxylic acids [2-6], acid hydrolysis yielded succinaldehydic acid. We were able to recover the latter as a monomer from its sulfuric acid solution. The yield of the crude acid was 53% of the theoretical. Its trimer has been prepared in an analytically pure state [8]. Hydrolysis in an alkaline medium yielded the expected 2-ethoxycyclopropane-1-carboxylic acid (II); exceptional precautions, such as described for its homolog [4], were required to recover it from the alkaline solution owing to its slight stability in the presence of hydrogen ions (also see the experimental section below). The acid yield was 85% of the theoretical.

$$(I) \xrightarrow{H_2SO_4} 2C_2H_5OH + OCH-CH_2-CH_2-CO_2H \longrightarrow (C_4H_6O_3)_3 \qquad (3)$$

$$(I) \xrightarrow{NaOH} C_2H_5OH + \underset{(II)}{C_2H_5O-CH\!\!-\!\!CH-COOH} \qquad (4)$$
$$\qquad\qquad\qquad

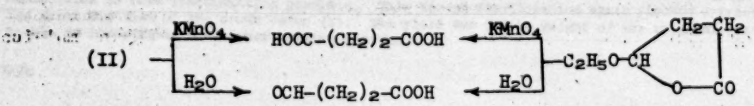
According to Rambaud, on the other hand, even the freshly prepared acid has an excessively high equivalent (133.0) when the determination is made by direct titration with 0.1 N $Ba(OH)_2$; back titration, however, yields a value that is close to the calculated one (129.75). He states that keeping the acid for two months in a closed vessel results in so great a rise in the equivalent (direct titration yielded an equivalent of 500) that the liquid was no longer a representative acid, although it was neutralized by one hour's contact with an excess of barium hydroxide (back titration yielded an equivalent of 125). These observations led the French researcher to put forward the hypothesis that the isomeric lactone is present as an impurity even in the freshly prepared acid.



The percentage of this lactone rises continually when the acid is stored in a closed container, owing to the acid's marked tendency toward "spontaneous isomerization" [4] at room temperature. Rambaud also comments on the extraordinary ease with which the acid (II) oxidizes to succinic acid, not merely under the action of various oxidizing agents ($KMnO_4$, CrO_3, etc.), but even when a sample of the acid is exposed to the open air (for 5 days). This latter observation led Rambaud to assume that "the spontaneous isomerization (of the acid to the lactone – I.D.), which we propose to investigate in detail, is no doubt intimately linked to the conversion of the ethoxycyclopropanecarboxylic acid or of its ethyl ester into succinic acid." The "investigation in detail" did not follow, however, and the existence, as well as the structure, of the lactone remained essentially unproved, since the French chemist did not isolate the latter (in the pure state) or identify it.

In the present research, we have managed to come somewhat closer to a solution of this problem. Subjecting one of the preparations of the acid to repeated fractionation in vacuum, we noticed a rather perceptible change in the boiling point and in other constants, as well as a certain increase in the equivalent determined by direct titration. Several redistillations in vacuum resulted in the nearly complete isomerization of the acid into the lactone, which was isolated in an analytically pure state with a yield that was 50% of the theoretical, based on the original acid. Its composition and molecular weight were the same as those of the original acid, but its physical properties (boiling point, specific gravity, n_D^{20}) and its molecular refraction differed considerably from the respective constants and molecular refraction of the acid. A cold solution of 0.1 N NaOH does not affect the lactone upon instantaneous contact, though the latter does consume a titrated solution of the alkali when it is allowed to stand with an excess of the alkali; this occurs with especial ease upon heating. When we determined the equivalent by back titration, we secured values that were somewhat low (an equivalent of 126.5-127.1), the value for the acid (II) after storage in a closed vessel (an equivalent of 125) being the same as that secured in the cited experiment of Rambaud's (see above).

Hydrogen does not attack the lactone in the cold with platinum black present. Like its isomeric acid (II), the lactone is readily hydrolyzed by 20% acetic acid, yielding succinaldehydic acid and ethyl alcohol. The acid and the lactone are both oxidized to succinic acid by a solution of potassium permanganate in the cold.



(II) (III) (5)

The formula for the lactone given above (III) has a structure that differs from that proposed by Rambaud (vide supra). We believe that Rambaud's formula must be rejected as not conforming to the equation for the reaction cited above [4]. Nor can Rambaud's formula be reconciled with his own hypothesis, which admits of the existence of a relationship between the oxidation of the acid (II) to succinic acid and its "spontaneous isomerization" to the lactone. The fact that the products of the conversion of the acid (II) are the same as those of the conversion of the lactone (III) in identical reactions support the hypothesis that the lactone (III) is formed as an intermediate phase in the hydrolysis and oxidation of the acid (II). This opinion is not a definite one, however, in view of the amount of research still to be done on the mechanism involved in both reactions.

EXPERIMENTAL

I. Ethyl Ester of 2-Ethoxycyclopropane-1-carboxylic Acid (I)

A. Synthesis of the ester with purified ethyl diazoacetate and $CuSO_4$.

The crude ethyl diazoacetate was purified by steam distillation in vacuum above barium hydroxide, as specified by Gatterman – Wieland [9]. The ethyl vinyl ether, the commercial product produced by the Favorsky-Shostakovsky method [10], was shaken up several times with a dilute solution of potash to eliminate any traces of ethyl alcohol, desiccated with fused potash, and fractionated into a column. B.p. 36°. The catalyst used was anhydrous copper sulfate.

0.3-0.4 g of the catalyst and 100-140 ml of the vinyl ethyl ether were placed in a reaction flask. A mixture of approximately equal volumes of ethyl diazoacetate and the vinyl ether was transferred to a dropping funnel, the reaction flask was heated until the ether began to boil, and the solution of ethyl diazoacetate was gradually added drop by drop. As a rule, the evolution of nitrogen begins after about 1/3 to 1/4 of the solution has been added. The entire process, during which nearly the quantitative amount of nitrogen is evolved, takes some 3 to 4 hours. The end of the reaction is indicated by a change in the evolution of the nitrogen; this usually occurs after the mixture has been heated for 30-40 minutes. After the solution had cooled, the partially changed catalyst (blackened) was filtered out, and the unreacted vinyl ether was driven off over a water bath, the residue being then distilled in vacuum; we collected a fraction within 3 to 4° intervals, the constants of which approximated those of the pure ester (I) (cf I, E): b.p. 71-73.5° at 9 mm; d_4^{20} 0.9868; n_D^{20} 1.42485.* The ester usually contained 2-3% of an ester of fumaric acid (Table 5). The numerical data on the foregoing synthesis are listed in Table 1. The lower yield obtained in Test 3 was apparently due to the harmful effect of the length of the run, which favored the formation of tar.

B. Synthesis of the ester with crude ethyl diazoacetate and $CuSO_4$

The apparatus and the experimental conditions were the same as in I, A. The course of the reaction, however, was quite different from that described in I, A, the "latent" period of the reaction (i.e., until nitrogen begins to be evolved) being much longer. In one of the runs the reaction was highly exothermic even

*In addition to the principal fraction, distillation usually yielded a fraction with a b.p. of 74-80° at 9 mm (5-10% by weight of the main fraction). This fraction was refractionated as soon as enough of it had been accumulated to make fractionation possible. This second fractionation again yielded a fraction whose boiling point was that of the crude ester (I). The yield was 50% by weight of the original fraction; we were unable to investigate the higher-boiling residue.

TABLE 1

Synthesis of Ester (I) with Purified Ethyl Diazoacetate and $CuSO_4$

Test No.	Reagents				Duration, hours	Reaction product: Ester (I)	
	Vinyl ether, ml		Ethyl diazoacetate (g)	$CuSO_4$ (g)		Boiling point	Yield, % theoretical
	In the reaction flask	In the dropping funnel					
1	140	47	46	0.4	4	71-75° at 9 mm	70.0
2	110	47	46	0.4	3	71-73.5 at 9 mm	69.8
3	100	36	38	0.3	6	64-67 at 7 mm	63.0

after practically all the ethyl diazoacetate had been added, though almost no nitrogen had been evolved up to that point. The reaction involved considerable tarring, and the yield of the reaction product was lower than in the tests run with pure ethyl diazoacetate. The crude ester was highly contaminated with high-boiling fractions, from which ethyl fumarate was recovered. Table 2 gives the results of two test runs with crude ethyl diazoacetate. The columns headed "Reaction product" contain data on the characteristics of the two fractions collected during the first (coarse) fractionation of the reaction product. The constants of Fraction 1 (boiling point and n_D) are those of the crude cyclic ester described in I, A.

TABLE 2

Synthesis of the Ester (I) with Crude Ethyl Diazoacetate

Test No.	Reagents				Reaction product			
	Vinyl ether, ml		Ethyl diazoacetate, (g)	$CuSO_4$ (g)	Fraction I		Fraction II	
	In the reaction flask	In the dropping funnel			Boiling pt. and n_D	Weight (g)	Boiling pt.	Weight (g)
1	100	40	38	0.3	83-85° at 16 mm, n_D^{20} 1.428	20.9	85-98° at 16 mm	7
2	100	40	30	0.3	73-77° at 12 mm, n_D^{20} 1.427	16.6	77-98° at 12 mm	6

The second fractions collected in both of the runs listed in Table 2 were combined and refractionated into a vacuum column with a 30-cm herringbone dephlegmator. This fractionation yielded: 1) 6.4 g of the crude ester (I) with a b.p. of 73-77° at 12 mm; $n_D^{20.1}$ 1.428; and 2) 3.5 g of ethyl fumarate, with a b.p. of 97.5-99° at 13 mm; d_4^{20} 1.0498; n_D^{20} 1.439. The small amount of the fumaric ester at our disposal did not allow us to isolate the ester in a perfectly pure state. The figures in the literature, however, differ but little from those cited above: b.p. 99° at 12 mm or 98-99° at 14 mm; d_4^{25} 1.0472; n_D^{20} 1.441 [11]. For convincing proof of the identity of the ester we had recovered, it was saponified with an alcoholic solution of potassium hydroxide to fumaric acid, which had a m.p. of 274° in a sealed capillary after crystallization from water. The figures in the literature are: m.p. 273° [12], 283° [13], and others (lying within these limits [11]). A test sample, mixed with known fumaric acid (m.p. 280° fused between 274° and 280°. The yield of the crude

ester (I) was 43.9 g, or 43.4% of the theoretical, based on the aggregate charge of ethyl diazoacetate in both tests. The yield of the pure cyclic ester, prepared from the crude by treating the latter with a cold solution of 3.4 g of potassium permanganate (I, E), was 32.5 g, or 33.13% of the theoretical. B.p. 68-72° at 8 mm. It does not decolorize an alkaline solution of permanganate.

C. Synthesis of ester (I) with Natur Cupfer C in ligroin *

Table 3 indicates that the constants of the reaction product are even closer to those of ethyl fumarate, which are listed in Column 8 for the sake of comparison, than to those of the ester (I) (Column 9).

TABLE 3

Ligroin	Vinyl ethyl ether, g	Ethyl diazo-acetate, g	Cu, g	Length of run, hours	Reaction product: Yield, g	Measured constants	Constants of ethyl fumarate	Constants of ester (I)
50	6.5	5	0.1	0.5	2	B.p. 105-115° at 20 mm $d_4^{17.5}$ 1.035 $n_\alpha^{17.5}$ 1.434	98-99° at 14 mm $d_4^{16.6}$ 1.0537 n_α^{15} 1.438	73-75° at 12 mm d_4^{20} 0.9854 n_α^{20} 1.425

D. Synthesis of ester (I) with Natur Cupfer C in vinyl ether and ligroin

We see from Table 4 that the constants of the reaction product are satisfactory and its yield is 40-48% of the theoretical when the reaction is carried out in vinyl ether plus ligroin (approximately 1:1 by volume).

TABLE 4

Test No.	In the reaction flask: Ligroin ml	Vinyl ethyl ether, ml	Catalyst g	In the dropping funnel: Ethyl diazo-acetate g	Vinyl ethyl ether ml	Ligroin ml	Duration of run, hours	Reaction product: Ester (I) B.p. and pressure	n_α^{20}	Yield % theor.
1	95	80	0.5	30	30	–	8	68-72° at 9 mm	1.425	48
2	120	100	0.5	38	20	18	9	69-72° at 9 mm	1.425	40

E. Purified Ester (I)

The crude ester (I) was shaken up with a 3% solution of potassium permanganate in a bottle with a ground-glass stopper until the purple coloring of the solution no longer disappeared. The manganese dioxide was then filtered out, and the permanganate ion was eliminated from the solution, after which the purified ester

* The apparatus used and the synthesis conditions were the same as in I,A or I,B. The ligroin was purified as follows: A gasoline fraction with a b.p. of 80-100° was repeatedly agitated with concentrated sulfuric acid to free it of unsaturated compounds; then it was washed with a soda solution and with water until its reaction was neutral, desiccated, and distilled. This purified ligroin must not decolorize a permanganate solution.

was separated from the aqueous layer, which was extracted with sulfuric ether. An ethereal extract was also made of the manganese dioxide. The ether extracts were combined with the bulk of the ester, which was then desiccated above sodium sulfate and distilled in vacuum after the solvent had been driven off (Table 5).

B.p. 68.5-70° at 8 mm; d_4^{20} 0.9854; d_4^0 1.0030; n_α^{20} 1.425. MR_α 41.03; computed 39.96.

0.1457 g substance: 0.3230 g CO_2; 0.1171 g H_2O. 0.1848 g substance: 0.4140 g CO_2; 0.1528 g H_2O. 0.1947 g substance; 15.97 g benzene: Δ t 0.395°. 0.3635 g substance: 15.97 g benzene: Δt 0.725°. Found %: C 60.46, 61.09; H 8.99, 9.25; M 159.0, 161.6. $C_8H_{14}O_3$. Computed %: C 60.76; H 8.86; M 158.1.

Rambaud's data: b.p. from 74-75.5° to 77-77.5° at 13 mm; d^{18} from 0.0982 to 0.995; n_D^{18} 1.4285-1.4295.

The raman spectrum of the ester (I) was recorded with a Zeiss triple-prism spectrograph. The excitation source was a mercury lamp (λ 4358.3 A); the slit width was 0.1 mm; the exposure was 9 hours. The light filter was a yellow glass, which weakened the intensity of the violet line. The results of our measurement of the spectrum of the ester (I) were as follows: 721(3); 751(0.5); 858(5); 953(2); 996 (0.5); 1042(3); 1111(1); 1187(0.5); 1218(0.3); 1296(1); 1360(1); 1395(2); 1446(5); 1723(3); 2875(5); 2931(2); 2980(2); 3015(2); 3049(1); 3069(1).

TABLE 5

Purification of the Crude Ester

Test No.	Reagents		Purified Ester (I)			Per cent of ethyl fumarate, by weight of the crude ester
	Crude Ester (I), g	$KMnO_4$ (g)	B.p. at 9 mm	Yield, % of theory		
				Based on the crude ester (I)	Based on the ethyl diazoacetate	
1	44.6	3	70-72°	86	60.2	2.5
2	107.0	7	68.5 - 70.5	90	63.0	3.1

Note 1. The data in Table 5 refer to the purification of the crude ester prepared by the method described in I, A. The yield of the pure ester is based on the crude ester as well as on the compound originally used in synthesizing the latter: the ethyl diazoacetate. In the latter case, it has been assumed that the yield of the crude ester was 70% of the theoretical, based on the ethyl diazoacetate.

Note 2. If we assume that the unsaturated compounds present as impurities in the crude ester are ethyl fumarate (I, B), the percentage of this ester in the crude preparation may be calculated approximately from the amount of permanganate used in oxidizing it. The calculation is based on the assumption that 1 mole of fumarate is oxidized by the permanganate solution to 2 moles of acetic and 2 moles of oxalic acids. The results of this calculation are listed in Column 7.

F. Cleavage of the ester (I) by oxidation

5 g of the purified ester (I) and 100 ml of a 3% solution of $KMnO_4$ were heated together to 90° over a water bath, with mechanical stirring, until the solution was decolorized. Oxidation was then effected with dry pulverized permanganate, which was added to the heated solution in 3-gram batches. A total of 16.5 g of permanganate was used [Equation (2) calls for 16.7 g of $KMnO_4$]. The solution was

processed in the usual manner and then distilled, a p-nitrophenylhydrazine test of the distillate indicating that the latter contained no neutral oxidation products. The solution left in the distilling flask was acidulated with the requisite amount of sulfuric acid and distilled with steam. The distillate required 298 ml of 0.1 N NaOH for neutralization, equivalent to a yield of 2.23 g of acetic acid (60% of the theoretical). The neutralized solution was evaporated over a water bath and then precipitated with silver nitrate. The silver salt was divided into two fractions and analyzed for its silver content:

Fraction I: 0.1008 g substance: 0.0651 g Ag. Fraction II: 0.1367 g substance: 0.0878 g Ag. Found %: Ag 64.42, 64.23; $C_2H_3O_2Ag$. Computed %: Ag 64.66.

Ether extraction of the acid solution left in the distilling flask yielded 1.2 g of succinic acid (33% of the theoretical). It fused at 184° after crystallization from water, the same melting point as that of a test sample of the acid mixed with known succinic acid.

0.1472 g substance: consumed 24.6 ml 0.1 N NaOH. 0.1584 g substance: consumed 26.5 ml 0.1 N NaOH. Found equivalent: 59.79, 59.66. $C_2H_4(COOH)_2$. Computed equiv. 59.05.

G. Hydrolysis of the ester (I) in an acid medium

15.8 g of the ester (I) was boiled for 1 hour with 100 ml of 10% sulfuric acid, the solution being stirred rapidly. After hydrolysis was over, 17.5 g of $BaCO_3$ was added to the solution to bind most of the sulfuric acid (19.5 g of $BaCO_3$ are called for theoretically for complete neutralization), and the precipitate of barium sulfate was suction-filtered out. The sulfuric acid left in the solution was neutralized with a solution of barium hydroxide, which was added a drop at a time until no more $BaSO_4$ was precipitated.* Then the solution was refiltered, and the filtrate was evaporated to dryness in vacuum over a water bath. The residue left after the water had been driven off consisted of a viscous yellowish liquid weighing 7.8 g. The liquid was distilled in 7-8 mm vacuum, yielding 5.4 g (53% of the theoretical yield) of succinaldehydic acid, with a b.p. of 126.5-127.5° at 7 mm. The acid was rose-colored; the color was eliminated by by redistillation, though this resulted in a reduction of the yield and a change in the boiling point, owing to the tendency of the acid to polymerize and oxidize.

B.p. 127-132° at 8 mm; d_4^{19} 1.163; n_D^{19} 1.458; MR_D 22.05; computed 22.19.

0.2207 g substance: consumed 19.5 ml 0.1 N NaOH. 0.2273 g substance: consumed 20.3 ml 0.1 N NaOH. Found equiv. 113.2, 112.0. $C_4H_6O_3$. Computed equiv. 102.0.

Comparison of these constants with the constants given in the literature for succinaldehydic acid [6,8] and of the observed equivalent with the computed value indicated that the synthesized acid was not pure enough. Its identity was proved by converting the acid into the solid trimer, the melting point of which was 147-148° (the capillary being heated slowly) after crystallization from water, which agrees with the figure in the literature [6,8].

II. 2-Ethoxycyclopropane-1-carboxylic Acid (II)

A. Hydrolysis of ester (I) in an alkaline medium. a) A mixture of the ester (I) with a 20% alcoholic solution of potassium hydroxide was allowed to stand overnight at room temperature, the reaction being completed the next day by heating for a brief time; b) a mixture of the ester (I) with a 5-10% aqueous solution of

*Care must be taken to secure complete elimination of the sulfate ion from the solution in the synthesis of succinaldehydic acid.

potassium hydroxide was boiled and stirred mechanically until the solution clarified. In each case the solution was neutralized with 10% sulfuric acid against phenolphthalein after hydrolysis was complete, and then concentrated to small volume over a water bath. The organic acid (II) was isolated by means of 10% sulfuric acid, which was added from a pipet to the chilled salt solution beneath a layer of sulfuric ether that had been poured on top of the solution. The organic acid was transferred to the ether layer by shaking, the ether layer was separated, and the foregoing operation was repeated with new batches of sulfuric acid and ether until all the sulfuric acid called for by calculation had been added (also see [4]). The combined ether extracts were desiccated with anhydrous sodium sulfate, the ether was driven off, and the acid residue distilled in vacuum. The results of two tests of the alkaline hydrolysis of ester (I) are listed in Table 6. The use of an alcoholic alkali yielded better results than an aqueous alkali (cf the yields and the boiling points of the acid produced in Tests 1 and 2).

TABLE 6

Hydrolysis of the Ester (I) in an Alkaline Medium

Test No.	Ester (I) (g)	Potassium hydroxide, g	Solvent	Amt. of solvent ml	Yield of Acid (II) Grams	% of theoretical	Boiling point of acid (II) and pressure
1	31.6	18	Alcohol	75	22.1	85.0	115.5-117° at 9 mm
2	66.3	38	Water	350	38.0	69.7	112.5-115.5° at 8 mm

Constants of acid (II):

B.p. 115-115.5° at 9 mm; d_4^{20} 1.079; $d_4^{23.3}$ 1.073; n_α^{20} 1.441; n_D^{20} 1.443; MR_D 31.96, MR_α 31.83; computed MR_D 30.89, MR_α 30.75.

(Rambaud's data [1]: B.p. 122° at 14 mm; $d_4^{18.5}$ 1.084; n_D^{18} 1.445; MR_D 31.90, computed 30.89).

0.1480 g substance: 0.2993 g CO_2; 0.0977 g H_2O. 0.1823 g substance: 0.3679 g CO_2; 0.1253 g H_2O. 0.1724 g substance: 0.3080 g AgI (Zeisel). Found %: C 55.14, 55.04; H 7.39, 7.69; OC_2H_5 34.32. $C_5H_{10}O_3$. Computed %: C 55.33; H 7.76; OC_2H_5 34.65.

Equivalent of acid (II), a) Freshly distilled acid: b.p. 115-115.5° at 9 mm. 0.3094 g substance: consumed 23.9 ml 0.1 N NaOH direct titration). 0.3094 g substance: 35.4 ml 0.1 N NaOH ; consumed 11.6 ml 0.1 N HCl (back titration). Found: equiv. 129.5, 130.0. $(C_5H_9O)CO_2H$. Computed equiv. 130.1

b) The same preparation after standing for 6 months in a closed vessel:

0.2057 g substance; consumed 15.8 ml 0.1 N NaOH. 0.2471 g substance: consumed 18.9 ml 0.1 N NaOH. Found: equiv. 130.6, 130.8. $(C_5H_9O)CO_2H$. Computed equivalent 130.1.

c) Preparation with b.p. of 115.5-117° at 9 mm: d_4^{23} 1.073; n_α^{23} 1.440; n_D^{20} 1.443. 0.2971 g substance: consumed 22.25 ml 0.1 N NaOH. 0.2500 g substance: consumed 18.8 ml 0.1 N NaOH. Found: equiv. 133.5, 133.2. $(C_4H_9O)CO_2H$. Computed: equiv. 130.1. 0.3196 g substance: 36.1 ml 0.1 N NaOH: consumed 11.25 ml 0.1 N HCl (back titration). Found: equiv. 128.6. $(C_5H_9O)CO_2H$. Computed: equiv. 130.1.

Rambaud's data: Direct titration with 0.1 N $Ba(OH)_2$ (against phenolphthalein). Found: equiv. 133.00. Back titration with 0.1 N HCl (again phenolphthalein. Found: equiv. 129.75.

B. Oxidation of the acid (II) by atmospheric oxygen. When a small quantity of the acid (1.5 -2.5 g) was allowed to stand for many days in an open crystallizing dish, it was completely converted into succinic acid.

By potassium permanganate. 14.2 g of permanganate in aqueous solution was used to oxidize 5.4 g of the acid, as against the 13.1 g of $KMnO_4$ called for theoretically. Oxidation took place at room temperature, the bottle containing the reaction mixture being shaken up at intervals. The first 50 ml of permanganate was used up in 3 hours, after which the consumption of the oxidant slowed down progressively. The whole process took 5 working days. The recovery of the succinic acid from the solution paralleled the procedure described in I, E. A few tenths of a gram of succinic acid was recovered, fusing at 182-183° after double recrystallization from water. A test sample, mixed with known succinic acid, exhibited no depression.

C. Hydrolysis of the acid (II) in an acid medium. 8 g of the acid (II), 15 ml of glacial acetic acid, and 60 ml of water were boiled for 6 hours with a reflux condenser. Then the acetic acid and the water were driven off by heating the mixture in vacuum over a water bath; 9 g of residue was likewise distilled in vacuum by heating over Wood's alloy. The resulting succinaldehydic acid was identified as follows:

B.p. 122-123° at 6 mm; d_4^{20} 1.269; n_D^{20} 1.458. MR_D 21.94; computed 22.19.

According to Harries and Himmelmann [8]: d_4^{23} 1.273; n_D^{23} 1.457; MR_D 21.84.

0.1745 g substance: consumed 16.65 ml 0.1 N NaOH. 0.3501 g substance: consumed 33.55 ml 0.1 N NaOH. Found: equiv. 104.8, 104.3. $C_4H_8O_3$. Computed: equiv. 102.1. (according to Harries and Alefild: found equiv. 99.65).

Securing the succinaldehydic acid in the absolutely pure state is hampered by its tendency to oxidize and polymerize even when stored for a short time (cf Report V). Its solid trimer, on the other hand is fairly stable. The acid was converted into its trimer by adding a drop of concentrated H_2SO_4. Its m.p. was 148-150° (with the capillary containing the substance heated gradually) after crystallization from water; this agrees with the data in the literature. *

III. γ -Ethoxybutyrolactone (III)

38 g of the acid (II), with a b.p. of 112.5-115.5° at 8 mm (cf Table 6, Test 2) was desiccated with anhydrous sodium sulfate and then redistilled in vacuum: Fraction I – 102-112° at 8 mm, 3-4 g (a mixture of the lactone and the acid); Fraction II – 112.5-115.5° at 8 mm, 32 g; n_D^{20} 1.442. The neutralization equivalent for Fraction II was high, indicating the presence of the lactone as an impurity:

0.1019 g substance: consumed 6.5 ml 0.1 N NaOH. 0.1648 g substance: consumed 10.6 ml 0.1 N NaOH. Found: equiv. 155.6, 155.4. $(C_3H_6O)CO_2H$. Computed: equiv 130.1.

Refractionations in vacuum of Fraction II resulted in a progressive lowering of the acid's boiling point and refractive index. At the same time, the acid equivalent determined by direct titration was found to be high. The substance was fractionated in vacuum until a fraction with a constant boiling point, the lactone, was collected. The yield of the lactone was 18.7 g (about 50% by weight of the original acid). The rest of the substance consisted of an intermediate fraction (a mixture of the acid and the lactone), with a b.p. of 90-112° at 7 mm (totaling about 10 g) and a residue (2-2.5 g) of the hardly changed acid (b.p. 112-117° at 7 mm; n_D^{20} 1.442).

* The literature on the trimer is cited in Report V.

Constants and Analysis of the Lactone (III)

B.p. 86-86.5° at 6 mm; d_4^{21} 1.091; n_D^{21} 1.4334-1.4336; MR_D 31.00. $C_6H_{10}O_3$. computed: MR_D 31.00.

0.1250 g substance: 0.2532 g CO_2; 0.0852 g H_2O. 0.1469 g substance: 0.2972 g CO_2; 0.1028 g H_2O. 0.1887 g substance: 16.83 g C_6H_6: Δt 0.435°. 0.1537 g substance; 15.19 g C_6H_6: Δt 0.390°. Found %: C 55.24, 55.17; H 7.63, 7.83. M 133.6, 133.4. $C_6H_{10}O_3$. Computed %: C 55.38; H 7.76; M 130.1.

Equivalent (back titration)

An exactly weighed amount of the lactone was heated with an excess of 0.1 N NaOH, which was back titrated with 0.1 N HCl.

0.2764 g substance: consumed 34.50 ml 0.1 N NaOH; 11.70 ml 0.1 N HCl.
0.2863 g substance: consumed 34.50 ml 0.1 N NaOH; 11.85 ml 0.1 N HCl.
0.1687 g substance: consumed 17.23 ml 0.1 N NaOH; 4.25 ml 0.1 N HCl.
0.1435 g substance: consumed 16.57 ml 0.1 N NaOH; 5.29 ml 0.1 N HCl.
Found: equiv. 126.9, 126.4, 126.5, 127.1.
$(C_5H_9O)CO_2H$. Computed; equiv. 130.1.

The lactone (III) was distilled several times in order to secure a purer substance; we were unable to secure better titration results, however (also see Rambaud's figures, quoted on Page 923). When the lactone was heated for a brief period of time with p-nitrophenylhydrazine dissolved in acetic acid, it was cleaved, yielding the p-nitrophenylhydrazone of succinaldehydic acid. M.p. 176° after crystallization from water. It exhibited no depression of the melting point when mixed in a test sample with the known preparation (m.p. 176-177°). The action of hydrogen upon the lactone in the presence of platinum black, alkali, or an aqueous solution of potassium permanganate has been described in the introduction to this report.

SUMMARY

1. A study has been made of the reaction of ethyl diazoacetate and vinyl ethyl ether above copper catalysts, and a new method has been elaborated for the synthesis of the ethyl ester of 2-ethoxycyclopropane-1-carboxylic acid, that is much superior to the method developed by Rambaud.

2. Some of the reactions of the ethyl ester of 2-ethoxycyclopropane-1-carboxylic acid have been investigated, and its Raman spectrum has been recorded.

3. 2-Ethoxycyclopropanecarboxylic acid has been synthesized and investigated. In the course of this investigation, Rambaud's figures have been corrected.

4. A study has been made of γ-ethoxybutyrolactone, synthesized by isomerizing 2-ethyoxycyclopropane-1-carboxylic acid.

LITERATURE CITED

[1] Rambaud, Bull. Soc. chim., (5), 5, 1560 (1938).

[2] I.A.Dyakonov, J.Gen.Chem. 19, 1891 (1949). *

[3] I.A.Dyakonov, J.Gen.Chem. 20, 2290 (1950). **

[4] I.A.Dyakonov, J.Gen.Chem. 19, 2057 (1949). ***

[5] I.A.Dyakonov and N.A.Lugovtsova, J.Gen.Chem. 20, 12038 (1950).****

* See CB translation p. a-355 ff.
** See CB translation p. 2385 ff.
*** See CB translation p. a-527 ff.
**** See CB translation p. 2109 ff.

[6] I.A.Dyakonov and N.A.Lugovtsova, J.Gen.Chem. 20, 2048 (1950).

[7] Loos, J. prak. chem. (2), 79, 509 (1909).

[8] Harries and Alefeld, Ber., 42, 159 (1909); Harries and Himmelmann, Ber., 42, 166 (1909).

[9] Gattermann-Wieland. Practical Methods of Organic Chemistry (Russ. Ed.), 317. (1948).

[10] M.F.Shostakovsky and N.F.Bogdanov, J.Gen.Chem. 12, 249 (1942).

[11] Beilstein.

[12] Viseur, Bull. Soc. Chim. Belg., 35, 437.

[13] Weiss, Dauns, J.Am.Chem.Soc., 45, 1004.

[14] Volkenshtein, Yelyashevich, and Stepanov. Molecular Vibrations. (1950).

[15] Hibben and Teller, Raman Effect (1939).

[16] Lespieau, Bourguel, et Wakeman, Bull. Soc. Chim. (4), 51, 400 (1934).

[17] Rambaud, Comptes rend., 209 2089 (1935).

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REACTIONS OF ALIPHATIC DIAZO COMPOUNDS WITH UNSATURATED COMPOUNDS

VIII. THE REACTION OF ETHYL DIAZOACETATE WITH ALLYL BROMIDE

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In previous reports of this series [1,2,3] one of the present authors has described syntheses of some derivatives of cyclopropane, using ethyl diazoacetate, and made a study of the properties and transformations of these derivatives:

$$CH_2{=}CH{-}OR + N_2CH{-}COOC_2H_5 \xrightarrow[(CuSO_4)]{Cu} CH_2\!\!<\!\!\begin{matrix}CH{-}OR\\ CH{-}COOC_2H_5\end{matrix} + N_2$$

$R = OC_2H_5$, OC_4H_9, $OCOCH_3$.

In the present research we proposed to carry out an analogous reaction between allyl bromide and ethyl diazoacetate:

$$CH_2{=}CH{-}CH_2Br + N_2CH{-}COOC_2H_5 \xrightarrow[(CuSO_4)]{Cu} Br{-}CH_2{-}CH\!\!<\!\!\begin{matrix}CH{-}CO_2C_2H_5\\ CH_2\end{matrix} + N_2$$

with the aim of effecting a further transformation to compounds of this type:

$$R{-}O{-}CH_2{-}CH\!\!<\!\!\begin{matrix}CH_2\\ CH{-}COOC_2H_5\end{matrix}$$

This latter reaction turned out altogether differently, inasmuch as the end product of the reaction of allyl bromide with ethyl diazoacetate was an acyclic ester:

$$CH_2{=}CH{-}CH_2{-}CHBr{-}COOC_2H_5.$$

(I)

This singular result may be interpreted in two ways.

The first hypothesis presupposes that the expected cyclic ester is formed at first, subsequently being isomerized under the reaction conditions to the unsaturated ester (I), the halogen atom being shifted to the beta position and the ring being ruptured.*

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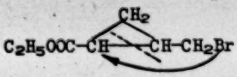
*As long ago as 1939 Academician A. E. Favorsky pointed out the possibility of an isomerization of this sort in the trimethylene series, similar to the allyl rearrangement of halogen derivatives, in connection with the following reaction observed by one of the authors of the present paper [4]:

$$CH_3CO{-}CH\!\!<\!\!\begin{matrix}CH_2\\ CH_2\end{matrix} + PCl_5 \rightarrow CH_3{-}CCl_2{-}CH\!\!<\!\!\begin{matrix}CH_2\\ CH_2\end{matrix} \longrightarrow CH_2{-}CCl{=}CH{-}CH_2{-}CH_2Cl$$

(A) (B)

(continued on next page)



(I)

The second possibility is that the reactive "C—Br" bond in the allyl bromide is directly attacked by the "free" carbethoxymethylene "$>CH-COOC_2H_5$", formed by the decomposition of the ethyl diazoacetate in the presence of copper. If this latter conjecture is right, then the hypothesis we had previously advanced regarding the participation of methylene and its substitutes in the reactions of unsaturated compounds with diazo compounds would receive further confirmation, as it were, since the intermediate formation of pyrazolines is obviously inapplicable to this case [5].

At the present time none of the proposed explanations has adequate proof, but we believe that experimental proof may be adduced in the future in support of one of them, provided an analogous reaction can be effected between ethyl diazoacetate and allyl halogen derivatives of more involved structure. No matter which of these mechanisms may finally prevail, moreover, we believe that the reaction we have carried out is quite novel, inasmuch as there is no reference in the literature to the ability of aliphatic diazo compounds to react with alkyl halides under any conditions. * Furthermore, if we succeed in applying this synthesis to other compounds, it may be expected that it will attain preparative importance in the future whenever the need arises of producing esters of unsaturated α-bromoacids or of the respective α-hydroxy acids, esters of unsaturated acids, and other compounds (vide infra).

In the research reported on in the present paper we have synthesized the following compounds not hitherto described in the literature, by means of simple reactions and with fairly high yields:

1) The ethyl ester of α-bromoallylacetic acid (I) – in a condensation reaction – the yield being 68-74% (the yield of the crude product, containing traces of isomeric esters, was 83.5-97% of the theoretical).

2) α-Hydroxyallylacetic acid (III) – by saponifying the ester (I) – the yield being 60% of the theoretical.

Moreover, the ethyl ester of allylacetic acid (II) has been synthesized with a yield of 50% of the theoretical by reducing the ester (I) with zinc dust in acetic acid (the yields given in the literature for this ester, produced by other methods, do not exceed the value given here), while hydrogenation of the acid (III) with platinum has yielded n-α-hydroxyvaleric acid (IV), the yield being 93% of the theoretical.

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*(continued from previous page)

The unsaturated dichloride (B) was synthesized instead of the expected cyclic dichloride (A). It should be pointed out, however, that the rearrangement of a cyclic bromide formed in the reaction of allyl bromide with ethyl diazoacetate is not quite the same as the transformation previously observed in the reaction with acetyltrimethylene.

Whereas the centers of the rearrangement and substitution reactions coincide in the latter case (the dichloride A), the rearrangement cannot be occasioned by the reaction in the hypothetical cyclic bromide, since the rearrangement center is unaffected by the reaction.

*In contrast to the reaction we have observed, the reaction described by Nierenstein [6], involves the interaction of acid halides with diazomethane:

$$R\text{-}COCl + CH_2N_2 \longrightarrow R\text{-}COCH_2Cl + N_2.$$

and apparently involves an entirely different mechanism, since its intermediate products are diazo ketones (Arndt, Eistert [7]), which can be readily recovered by using an excess of diazomethane in the reaction:

$$RCOCl + 2CH_2N_2 \longrightarrow RCO\text{-}CHN_2 + CH_3Cl + N_2.$$

The complicated researches involved in determining the structure of the ester (I) are set forth in the experimental section of this paper. The principal difficulties were occasioned by the fact that it was hard to forsee the end product in view of the large number of possible courses the reaction could take. The cyclic formula was rejected after the ester was proved to be unsaturated with respect to permanganate, which oxidized it to oxalic and acetic acids. The refraction data indicated that it possessed one double bond. The unsaturated isomers (1–6) and (I) of this ester, illustrated below, were considered to be possible products of its rearrangement during the reaction. We also bore in mind the allyl isomers (2a) and (6a) of the isomers (2) and (6):

(1a) $CH_2Br-CH_2-CH=CH-COOC_2H_5$

(2) $CH_2Br-CH=CH-CH_2-COOC_2H_5$

(2a) $CH_2=CH-CHBr-CH_2-COOC_2H_5$

(3) $CH_2Br-CH_2-C(=CH_2)-COOC_2H_5$

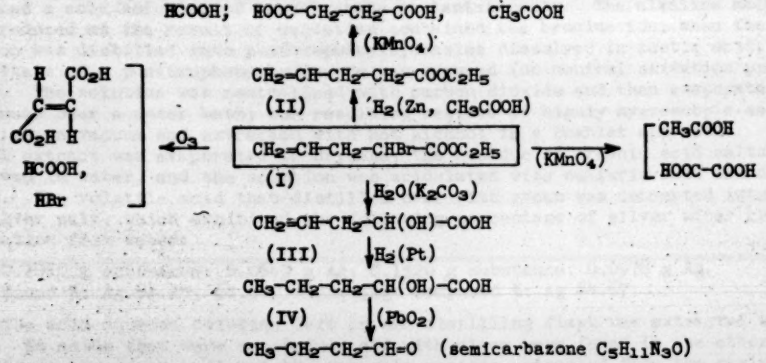
(4) $CH_2Br-CH=C(CH_3)-COOC_2H_5$

(5) $CH_2Br-C(=CH_2)-CH_2-COOC_2H_5$

(6) $BrCH_2-C(=CH_2)-CH=COOC_2H_5$

(6a) $CH_2=C(CH_3)-CHBr-COOC_2H_5$

The unequivocal choice of Formula (I) was based upon the concomitance of the various reactions that had to be employed to prove the structure of this ester. The basic outline of our experiments is represented by the following set of reactions:



The sequence of these reactions was as follows. A dehalogenation reaction (I → II) yielded the ester (II), the structure of which was proved by oxidizing it to succinic and acetic acids with permanganate. This result enabled us to ignore in our subsequent work the formulas for the branched-chain isomers (3-6) and (6a), as well as formula (1a). We still had to make a choice among the formulas (2), (2a), and (I). An ozonation reaction enabled us to show that the isomer 2 had to be rejected as well, inasmuch as neither acetic nor bromoacetic (nor glycolic) acid was found among the decomposition products of the ozonide, though formic and fumaric acids were found. The formation of fumaric acid instead of bromosuccinic acid, as called for by Formulas (I) and (2a), was no surprise to us, as we knew that when bromosuccinic acid is heated in aqueous solutions, it breaks down into a mixture of fumaric and malic acids.* The primary ozonation

*Decomposition of concentrated aqueous solutions yields more fumaric acid [6].

Fraction I,	69-78° at 12 mm,	- 8.6%	In % by wt.
Fraction II,	78-79° at 12 mm, n_α^{20} 1.46018	- 81.4	of the crude
Fraction III,	79-84° at 2 mm	- 10.0	ester

Characteristics of Fraction II. B.p. 74-75° at 10 mm; 76-77° at 11 mm; 78-79° at 12 mm; d_4^0 1.3315; d_4^{20} 1.3099; n_D^{20} 1.4642; n_α^{20} 1.4602; MR_D 43.63; MR_α 43.31. $C_7H_{11}O_2Br$. Computed MR_D 43.48; MR_α 43.10.

0.0959 g substance: 0.1431 g CO_2; 0.0451 g H_2O. 0.0983 g substance: 0.1470 g CO_2; 0.0489 g H_2O. 0.1724 g substance: 0.1574 g AgBr. 0.0893 g substance: 0.0811 g AgBr. 0.2390 g substance; 20.08 g C_6H_6: Δt 0.30°. 0.4010 g substance; 20.08 g C_6H_6: Δt 0.50°. Found %: C 40.69, 40.78. H 5.26, 5.56; Br 38.86, 38.64; M 203.5, 204.8. $C_7H_{11}O_2Br$. Computed %: C 40.59; H 5.35; Br 38.59; M 207.1.

The ester yield, based on Fraction II alone, was 97.03 g (68.11% of the theoretical). The yield may be raised to 74% of the theoretical by refractionating Fraction I, which apparently is a mixture of isomeric esters of the same composition.

Lastly, Fraction III, secured in the fractionation of the major reaction product, also seems to consist principally of the ester (I); the latter was not isolated in the pure state owing to the insufficient quantity of this fraction collected.

Oxidation of the ester (I) with potassium permanganate. The ester decolorized a cold solution of permanganate instantaneously. The alkaline solution produced as the result of oxidation contained the bromine ion; when the solution was distilled into p-nitrophenylhydrazine dissolved in acetic acid, no precipitate of a p-nitrophenylhydrazone was secured (no neutral oxidation products). The solution was neutralized with carbon dioxide and then evaporated to dryness over a water bath; the resulting residue of highly hygroscopic salts was dried in vacuum and extracted with hot alcohol in a Soxhlet apparatus. The alcohol extract was evaporated to dryness; the residue of organic acid salts was dissolved in water, and the solution was acidulated with sulfuric acid and distilled. The volatile acid that distilled over with steam was converted into its silver salt, which exhibited the following percentage of silver after crystallization from water:

0.1010 g substance: 0.0649 g Ag; 0.1520 g substance: 0.0978 g Ag. Found %: Ag 64.25, 64.34. $C_2H_3O_2Ag$. Computed %: Ag 64.67.

The acid aqueous solution left in the distilling flask was extracted with ether. No acids that were not driven off with steam were found in the ether extract; we therefore analyzed the dry salt residue extracted from the casing of the Soxhlet apparatus. The salts were dissolved in water, and the solution was acidulated and extracted with ether in an extractor. The ether extract yielded oxalic acid, identified by a test sample mixed with the known acid in a fusion test. M.p. 189-190° after sublimation.

Ozonation of the ester ($C_7H_{11}O_2Br$). 1) 10 g of the ester, 40 ml of $CHCl_3$, and 36.7 liters of 4% ozone. Ozonation lasted 5.5 hours. The ozonide was decomposed by heating it with water; the resultant solution was neutralized with soda and distilled with steam. We succeeded in recovering about 0.5 g of a light oil from the first runnings of the distillate by adding potash to it; the oil formed a silver mirror with ammoniacal silver nitrate and formed a p-nitrophenylhydrazone. The p-nitrophenylhydrazone fused at 144° after double crystallization from an alcohol-benzene mixture. The melting point of p-nitrophenylhydrazone acrolein is 151°.

0.0512 g substance: 9.6 ml N_2 (19°, 759 mm); 0.0697 g substance: 13.5 ml N_2 (21°, 740.8 mm). Found %: N 21.58, 21.59. $C_3H_9N_3O_2$. Computed %: N 21.91.

We were unable, however, to secure the semicarbazone, corresponding to acrolein.

The bromine ion was found in the solution left after the aldehyde had been distilled with steam. The color of the solution was dark. Evaporating it to dryness over a water bath yielded a dark, tarry mass of salts, which was extracted with hot alcohol in a Soxhlet apparatus. After extraction was complete, the alcoholic extract was evaporated to dryness, the organic salts in the residue were dissolved in water, the solution was acidulated with sulfuric acid, and the volatile acids were distilled with steam. No acids that were not volatile with steam were detected by extraction with ether. Formic acid was found in the distillate (recovery of calomel in the precipitate from a mercuric chloride solution in a separate test). The other acids that were volatile with steam were detected in the distillate by neutralizing the latter with alkali and heating it with an excess of silver nitrate until no more metallic silver was thrown down in the precipitate. The filtrate was then carefully concentrated in vacuum. No silver salts or other acids were found. Dissolving the salts extracted from the casing of the Soxhlet apparatus in water, and then acidulating the solution and extracting it for a long time with ether yielded a negligible amount of a solid yellowish acid that did not fuse up to 250°. This acid was investigated in Experiment II (vide infra).

2) 20 g of the ester dissolved in $CHCl_3$, 62.11 liters of 5.2% ozone. Ozonation lasted 9 hours. After the ozonide had been decomposed with water, the solution was neutralized with 0.3 N alkali, the titer of which was established by means of the acid later used for the recovery of the acid products of ozonation. The neutral solution was extracted with ether for many days in the extractor. The ether extract yielded a small quantity of a yellow oil that exhibited a positive reaction with Tollens reagent and distilled between 78 and 83° with considerable tarring of the bulk of the substance. The distillate was converted into a p-nitrophenylhydrazone that did not fuse at 320° and could not be purified by crystallization from various solvents. We were unable to investigate this p-nitrophenylhydrazone or its corresponding aldehyde.

The percentage of mineralized halogen was determined gravimetrically.

Found Br 6.4 g; Computed: Br 7.8 g.

Then the solution was acidulated with a sulfuric acid that had been titrated against the alkali originally used, the quantity of acid being that calculated to be enough to drive out of the salts only the organic acids, while leaving the hydrobromic acid in the combined state. The percentage of the latter acid in the solution was calculated from the data on the mineralized halogen. The acid solution was extracted with ether in the extractor, the ether extract yielding the organic acids free of the bromine ion. One of them, a solid yellow acid, was triply crystallized from water with charcoal,* which yielded nearly colorless crystals with a m.p. of 276° (in a sealed capillary). A test sample mixed with known fumaric acid (m.p. 280°) exhibited no depression.

0.1370 g substance: consumed 22.7 ml 0.1 N NaOH; 0.0479 g substance: consumed 8.69 ml 0.1 N NaOH. Found: equiv 60.7, 55.1. $C_2H_2(COOH)_2$. Computed: equiv. 58.3.

The weighed sample of the acid, neutralized with alkali, was converted into its silver salt. The salt was dried at 100°. The drying of the salt was done

*This involved large losses of the acid owing to adsorption (cf Shilov and Nekrasov [10].

with the utmost caution because of its explosiveness. *

0.0922 g substance: 0.0598 g Ag. 0.1217 g substance: 0.0790 g Ag. Found %: Ag 64.84, 64.91. $C_2H_2(COOAg)_2$. Computed %: Ag 65.40.

In addition to the fumaric acid, the extraction with ether likewise yielded a liquid acid with a b.p. of 100-110°, which threw down a calomel precipitate when reacted with a solution of mercuric chloride; this distillate therefore contained formic acid. The distillate was also found to contain the neutral substance containing a carbonyl group described previously (b.p. of the p-nitrophenylhydrazone 320°), while the distillation residue contained a small amount of fumaric acid (m.p. 277° in a sealed capillary).

II. Ethyl Ester of Allylacetic Acid

5 g of zinc dust was gradually added to a mixture of 10 g of the ester, 10 ml of alcohol, and 14 ml of 50% acetic acid, heated to 60° over a water bath. Then the reaction mixture was heated with a reflux condenser for another hour over the water bath. The solution was then filtered; the filtrate was saturated with anhydrous soda, leaving the reaction of the solution slightly acid, and then it was extracted with ether in an extractor. After extraction was complete, the ether extracts were again shaken up with a small amount of soda solution until their reaction was neutral and desiccated with sodium sulfate. The ether was driven off, and the residue distilled in vacuum. Fraction I – 23-43° at 14 mm, 0.8 g; Fraction II – 43-46° at 14-16 mm, 3 g; Fraction III was the nearly pure ethyl ester of allylacetic acid. The yield of 3 g was 50% of the theoretical. Its constants were as follows after repeated distillations of large quantities of the ester:

B.p. 40.5-41.5° at 12 mm; 44-45° at 15 mm; d_4^{20} 0.9054; d_4^0 0.9234; n_α^{20} 1.4144; n_D^{20} 1.4171. MR_α 35.40; MR_D 35.76. $C_7H_{12}O_2F$. Computed: MR_α 35.50; MR_D 35.71.

Literature data [12]: B.p. 44-45° at 14 mm; 39-40° at 8 mm.

The other constants have been determined for the ester of allylacetic acid for the first time.

0.1863 g substance: 0.4478 g CO_2; 0.1603 g H_2O. 0.0948 g substance: 0.2271 g CO_2; 0.0891 g H_2O. 0.2923 g substance; 13.59 g C_6H_6: Δt 0.90°. 0.5007 g substance; 13.59 g C_6H_6: Δt 1.39°. Found %: C 65.55, 65.33; H 9.66, 9.44; M 122.6, 128.6. $C_7H_{12}O_2$. Computed %: C 65.58; H 9.45; M 128.2

Oxidation of the ethyl ester of allylacetic acid (II). Oxidation of 5 g of the ester (II) in aqueous solution in the cold required 11.73 g of $KMnO_4$. No neutral products of oxidation were found (p-nitrophenylhydrazone test). The aqueous solution of the oxidation products was acidulated and then distilled with steam. Formic acid was found in the distillate (calomel method). The formic acid was eliminated from the distillate by heating the solution of acids neutralized with alkali, over a water bath with an excess of silver nitrate until no more metallic silver was thrown down in the precipitate (2 hours).

The silver acetate salt was secured by concentrating the filtrate in vacuum.

* There are assertions in the literature [11], that it is impossible to analyze silver fumarate in this manner because of its explosiveness, it being recommended that the analysis be carried out by converting the salt into silver chloride. Our experiments have demonstrated, however, that the results obtained thereby are hardly reproducible. In both instances the tests were made with known silver fumarate.

0.1133 g substance: 0.0732 g Ag. 0.0732 g substance: 0.0472 g Ag. Found %: Ag 64.60, 64.34. $C_2H_3O_2Ag$. Computed %: Ag 64.67.

Succinic acid was recovered by extracting an aqueous solution of the acids that were not volatile with steam in an extractor with ether. We secured 0.15 g of the acid with a m.p. of 182-183° after crystallization from water.

A test sample mixed with known succinic acid fused at the same temperature. The acid was converted into its silver salt to determine its neutralization equivalent.

0.1419 g substance: consumed 23.82 ml 0.1 N NaOH. Found: equiv. 59.5. $C_4H_8O_2$. Computed equiv. 59.0. 0.1133 g salt: 0.0733 g Ag. 0.1952 g salt: 0.1268 g Ag. Found %: Ag 64.69, 64.43. $C_4H_4O_2Ag_2$. Computed %: Ag 64.66.

III. α-Hydroxyallylacetic Acid.

64.4 g of the ethyl ester of α-bromoallylacetic acid (I) and 585 ml of a 10% solution of potassium carbonate were boiled with mechanical stirring until the ester layer had vanished entirely (4 hours)*. After hydrolysis was complete, the solution was concentrated to a volume of 200 ml and acidulated with sulfuric acid until its reaction with Congo red was slightly acid, so as to keep the hydrobromic acid in the combined state, and the precipitated mineral salts were filtered out. When the salts were dissolved in water, what was insoluble was a minute quantity of a rubbery polymer, apparently the polymer of vinylacrylic acid, formed by splitting HBr from the molecule of the original ester.

The filtrate, freed of its mineral salts, was placed in an extractor and extracted with ether for many hours. The ether extracts were well desiccated with sodium sulfate, and the ether was driven off; this yielded 24.1 g (63.4%) of the theoretical) of α-hydroxyallylacetic acid as a yellow oil that crystallized into a dense mass of easily fusible, yellowish crystals only after standing above sulfuric acid in vacuum. The α-hydroxyallylacetic acid consisted of colorless rhombic crystals with a m.p. of 37° after crystallization from a mixture of petroleum ether (2 parts) and sulfuric ether (1 part).

0.1426 g substance: 0.2695 g CO_2; 0.0902 g H_2O. 0.1757 g substance: 0.3346 g CO_2; 0.1087 g H_2O. 0.1826 g substance. consumed 15.71 ml 0.1 N NaOH; 0.2455 g substance: consumed 20.81 ml 0.1 N NaOH. 0.2003 g substance; 20.20 g CH_3COOH: Δt 0.34°; 0.2747 g substance; 20.20 g CH_3COOH: Δt 0.47°. 0.0887 g substance: 34.62 ml CH_4 (17°, 774.7 mm) [Terentyev and Shcherbakova]: 0.0592 g substance: 23.42 ml CH_4 (14°, 763.4 mm). Found %: C 51.33, 51.93; H 7.07, 6.90; equiv. 116.2, 117.4. M 113.7, 112.8; OH 29.01, 28.28. $C_5H_8O_3$. Computed %: C 51.72; H 69.4; equiv. 116.1; M 116.1; OH 29.31.

The silver salt of α-hydroxyallylacetic acid is decomposed at the instant of its formation in aqueous solution, metallic silver being thrown down in the precipitate.

Distillation of the acid in vacuum apparently involves the partial formation of a lactide; this, as we know, is characteristic of the structure of an α-hydroxy acid. We could check this by means of the results of direct titration of a weighed sample of the distilled acid with alkali and comparing them with the results of back titration of a weighed sample of the same acid heated with an excess of titrated alkali. Distillation of 1.3 g of the acid in a 7-mm vacuum yielded 1 g of a colorless, extremely viscous liquid with the following constants.

*The solution remained cloudy after saponification, owing to the precipitation of polymeric compounds.

d_4^{20} 1.1381; n_α^{20} 1.4621; MR_α 28.01; computed MR_α 27.88.

Determination of the acid equivalent: a) direct titration. 0.1795 g substance: consumed 12.6 ml 0.1 N NaOH. 0.1468 g substance: consumed 10.3 ml 0.1 N NaOH. Found: equiv. 142.7, 142.5. $(C_4H_7O)CO_2H$. computed equiv. 116.1.

b) Back titration: 0.1518 g substance; 26.2 ml 0.1 N NaOH (heating for 15 minutes); consumed 13.2 ml 0.1 N HCl. 0.1120 g substance; 7.9 ml 0.1 N NaOH (heating for 15 minutes): consumed 2.6 ml 0.1 N HCl. equiv. 116.7, 115.4. $(C_4H_7O)CO_2H$. Computed: equiv. 116.1.

It must be assumed that the lactide ring is unaffected by direct titration, though it is ruptured when heated with an excess of alkali, as was the case in back titration.

Hydrogenation of α-hydroxyallylacetic acid (III). The acid (III) was hydrogenated in ether solution with platinum black, in a hydrogenation apparatus. The results of 2 hydrogenation tests are listed in the table.

Hydrogenation of α-Hydroxyallylacetic Acid

Test No.	α-Hydroxyallyl-acetic acid, g	Platinum, g	Hydrogenation time, minutes	Hydrogen added		Yield of α-hydroxy-valeric acid	
				in ml	in %	g	%
1.	5	0.58	45	963.7 (16°, 769 mm)	95.5	4.7	92.91
2	6	0.58	70	1208.4 (17°, 753 mm)	97.3	5.7	93.44

The hydrogenation product, α-hydroxyvaleric acid, was recovered as an oil that crystallized in vacuum above sulfuric acid as a colorless mass of highly hygroscopic crystals with a m.p. of 34-35°. The melting point was determined by the method used by Fittig [13] for α-hydroxyvaleric acid (m.p. 34° according to the literature [13,14]).

0.1726 g substance: consumed 14.49 ml 0.1 N NaOH. 0.1472 g substance: consumed 12.55 ml 0.1 N NaOH. Found: equiv. 119.1, 117.2. $C_5H_{10}O_3$. Computed: equiv. 118.1.

Analysis of the silver salt. 0.1125 g substance: 0.0542 g Ag. 0.1154 g substance: 0.0556 g Ag. Found %: Ag 48.17, 48.18. $C_5H_9O_3Ag$. Computed %: Ag 47.94.

Oxidation of α-hydroxyvaleric acid (IV) with lead peroxide. 5.5 g of α-hydroxyvaleric acid (IV) was oxidized with 12 g of PbO_2 in a solution of 16.5 g of glacial acetic acid and 16.5 g of 25% phosphoric acid, the mixture being heated for 3 hours with a reflux condenser over a water bath. After the reaction was over, the lead oxide was filtered out and washed with warm water. The filtrate was combined with the wash waters and distilled with steam. The first runnings of the distillate, collected separately from the subsequent distillate, consisted of two layers: the lower one was an aqueous layer, and the upper was a highly mobile oil that exhibited the characteristic aldehyde reactions with Tollens reagent, with a solution of semicarbazide acetate, etc. The aldehyde, the yield of which was increased to 0.5-0.6 g by salting out with potash, was removed with a pipet and placed in a solution of semicarbazide acetate in 50% alcohol. The semicarbazone, recovered after the solvent had been driven off in vacuum, fused at 78°. Triple crystallization from benzene raised the melting point to 93-94°.

0.0510 g substance: 14 ml N_2 (21°, 769 mm). Found %: N 32.70. $C_5H_{11}ON_3$. Computed %: N 32.52.

The melting point of the semicarbazone of the oily aldehyde is 77° according to Harries and 96° according to Blaise [15]. The semicarbazone of the known oily aldehyde fused at 77° before crystallization from benzene and at 96° after triple crystallization. In neither case did a test fusion sample mixed with the semicarbazone secured in our oxidation experiment exhibit any depression.

SUMMARY

1. It has been shown that the hitherto unknown ethyl ester of α-bromoallylacetic acid may be synthesized with a yield that is 70% of the theoretical by reacting allyl bromide with ethyl diazoacetate in the presence of copper or copper sulfate. This reaction is the first instance of the reaction of aliphatic diazo compounds with alkyl halides.

2. The structure of the ester has been proved exhaustively by various methods; it has been shown that hydrolysis of the ester in an alkaline medium makes it possible to secure a 60% yield of the hitherto undescribed α-hydroxyallylacetic acid, while reducing the ester in acetic acid yields the ethyl ester of allylacetic acid, its yield being 50% of the theoretical.

3. The suggestion is advanced that further research on this reaction and applying it to other alkyl halides may make some of its syntheses preparative ones for the production of esters of unsaturated acids that are inaccessible by other methods, as well as their halogen and hydroxy derivatives.

LITERATURE CITED

[1] I.A.Dyakonov, J.Gen.Chem. 19, 1892 (1949).*

[2] I.A.Dyakonov, J.Gen.Chem. 20, 2289 (1950).**

[3] I.A.Dyakonov and N.A.Izgovtsova, J.Gen.Chem. 21, 839 (1951). ***

[4] I.A.Dyakonov, J.Gen.Chem. 10, 414 (1940).

[5] I.A.Dyakonov, J.Gen.Chem. 19, 1734 (1949). ****

[6] Nierenstein and co-workers, J.Chem.Soc. 107, 1941 (1915); J.Am. Chem.Soc., 47, 1728 (1925); 52, 1504 (1930).

[7] Arndt, Eistert, Ber., 61, 1118, 1949 (1928); cf also Organic Reactions (Russ. Ed.), Vol. I, p. 53, ed. Adams (1948).

[8] Muller, Suckert, Ber., 37, 2598 (1904).

[9] Bayer and Liebig, Ber., 31, 2104 (1898).

[10] Shilov and Nekrasov, J.Russ.Phys.Chem.Soc., 60, 103 (1928).

[11] Kekule, Strecker, Ann., 223, 187 (1884); Weiss, Downs, J.Am. Chem.Soc., 45, 2348 (1923).

[12] Philippi, Monatsh., 51, 277 (1930); Wolgemuth, Ann. chem. (9), 2, 322.

[13] Fittig, Donnenberg, ... Ann., 331, 132 (1904).

[14]. Backer, Mulder, Rec. trav. chim., 55, 357 (1936).

[15] Harries, Chem. Zentr., 1916, II, 992; Blaise, Bull. (4), 15, 666 (1914).

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THE KINETICS OF THE DEALKYLATION OF ISOPROPYLBENZENE ABOVE AN ALUMINOSILICATE CATALYST

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The only data published in the literature on the dealkylation of isopropylbenzene above natural or synthetic aluminosilicates are the descriptions of the few experiments performed by Moldavsky and Bezdel [1], Thomas, Hoekstra, and Pinkston [2], and Greensfelder and Voge [3], who found that isopropylbenzene decomposes smoothly, with practically no side reactions, into propylene and benzene at 400-500°. Mamedaliev [4] has reported the dealkylation of isopropylbenzene and on the side reaction involved in the dealkylation of di-isopropylbenzenes above natural aluminosilicates. We see, therefore, that there is no systematic information in the literature on the dealkylation of isopropylbenzene above aluminosilicate catalysts.*

Our research deals with the kinetics of the dealkylation of isopropylbenzene above an industrial aluminosilicate catalyst.

EXPERIMENTAL

Initial substance and experimental procedure. The isopropylbenzene was produced by alkylating benzene with isopropyl bromide in the presence of aluminum chloride. The synthesized product was fractionated into a rectifying column equal to 17 theoretical plates. B.p. (at 760 mm) 152.0°; d_4^{20} 0.8632; n_D^{20} 1.4920.

The experiments were run in an apparatus of the circulating type. The layout of the apparatus and the experimental procedure have been described in one of our previous papers [5]. We shall deal briefly with a few changes made in the layout and the procedure. The product was fed into the reactor from a mercury buret. The reactor used was a glass tube 20 mm in diameter, which was prolonged into a tube with a smaller diameter (5 mm) directly behind the catalyst bed. The gaseous products were collected in a graduated pipet with a capacity of approximately 700 ml. The temperature in the catalyst zone was measured by means of three nichrome-constantan thermocouples, one being placed in the upper layer, the second in the middle layer, and the third in the bottom layer of the catalyst bed.

Before the run was started, the catalyst was activated at 480-500° by passing air through the reactor at a rate of 200-300 liters per liter of catalyst per hour, after which nitrogen was blown through the system. Then the product was fed into the reactor at the required rate of flow from the mercury buret. The liquid products and the gas produced during the first 5 to 10 minutes were collected separately and were not analyzed, as a rule. The length of the runs ranged from 7.5 to 120 minutes. The volume of the gaseous products formed was measured every 3 or 5 minutes (with an accuracy of ± 2 ml) during the runs. The gas exhaust rate was practically constant throughout all the tests, the sole exception being the runs that lasted 2 hours, during which time the activity of the catalyst was observed to drop off somewhat. Whenever the volume of gas was measured,

* We learned of the papers by Topchieva and Panchenkova [12] after our own paper had gone to press.

every three or five minutes, we measured the temperature in the preheating zone and at the three specified points in the catalyst zone. Owing to the automatic temperature control, the use of good thermal insulation, and effective preliminary heating of the hydrocarbon vapors, the readings of the thermocouples inserted in the reaction chamber did not vary more than 2-3°. Nitrogen was blown through the system after the end of each run.

The gaseous products were subjected to low-temperature rectification in a copper column designed by the All-Union Research Institute for the Chemical Processing of Gases, while the liquid products were rectified in a laboratory column with the efficiency of 32 theoretical plates. The specific gravity, the n_D^{20}, the molecular weight, and the percentage of unsaturated hydrocarbons were determined for each of the fractions collected for the liquid products. The amount of coke was determined by weighing the activated catalyst before the start of the run and the spent catalyst after the run was over. To make sure that the temperature in the reaction zone remained constant, the volume of catalyst placed in the reactor was varied from 10 to 60 ml, depending on the volumetric rate at which the isopropylbenzene was fed into the reactor.

Experimental results. The experiments on the dealkylation of isopropylbenzene above an aluminosilicate catalyst were run at 300, 350, 400, and 450° at volumetric rates of flow ranging from 0.125 to 15 liters per liter of catalyst per hour. The material balance sheets for the various tests are listed in Table 1. Parallel tests were run to secure more dependable results and to accumulate adequate amounts of the gaseous and liquid products for analysis.

TABLE 1

Material Balance of Experiments on the Catalytic Cracking of Isopropylbenzene

Test No.	Temperature	Volumetric rate of flow, l. per l. catalyst per hour	Time, minutes	Per cent by weight			
				Gas	Catalyst	Coke	Residue in reactor and losses
27	300°	0.125	120	3.4	88.6	3.8	4.2
26	300	0.25	60	1.6	91.5	1.3	5.6
23	300	0.5	60	1.5	93.0	0.7	4.8
6	350	0.5	40	9.3	84.8	3.4	2.5
7	350	0.5	40	9.3	85.5	3.5	1.7
2	350	1.0	60	6.8	88.8	2.0	0.4
3	350	1.0	60	7.5	89.1	1.7	1.4
4	350	1.0	60	7.1	89.6	1.9	1.7
9	350	2.0	35	5.6	92.1	0.4	1.9
10	350	2.0	30	5.9	91.5	0.5	2.1
11	350	4.0	15	3.8	94.6	0.2	1.4
16	400	0.5	60	15.0	78.0	-	5.9
17	400	0.5	60	14.2	78.0	2.2	5.5
18	400	1.0	45	14.8	-	-	-
19	400	1.0	60	15.3	81.5	1.7	1.4
20	400	2.0	30	14.8	81.4	0.5	3.3
21	400	4.0	15	13.2	84.0	0.9	1.9
22	400	8.0	7.5	9.2	90.2	0.4	0.2
24	400	12.0	15.0	5.0	92.7	0.2	2.1
14	450	0.5	60	19.1	75.0	0.9	5.0
15	450	0.5	60	19.8	75.0	0.7	4.5
13	450	1.0	60	19.8	78.0	2.0	0.2
12	450	2.0	25	20.0	77.1	2.3	0.6
34	450	8.0	22.5	16.3	82.4	-	-
31	450	10.0	18.0	14.7	83.1	-	-
33	450	12.0	15.0	12.5	85.5	-	-
32	450	15.0	12.0	9.4	89.4	-	-

As the foregoing table indicates, the yield of liquid products dropped as the temperature was raised, the volumetric rate being kept the same, while that of the gaseous products rose. The yield of gaseous products was practically constant at 400 and 450° for long contact times (volumetric rates ranging from 0.5 to 2 liters per liter of catalyst per hour); this was evidence that the maximum conversion of the isopropylbenzene had been attained for the given temperature.

Dealkylation of isopropylbenzene above an aluminosilicate catalyst is attended by the formation of coke, the latter varying from 0.2 to 3.8%. Changes in the volumetric rate affected the coke yield at a given temperature appreciably. When the volumetric rate was raised from 0.5 to 4.0 liters per liter of catalyst per hour at a temperature of 350°, the coke yield dropped from 3.5% to 0.2%. The variation of the coke yield with the volumetric rate at 300, 350, and 400° is illustrated graphically in Fig. 1.

The composition of the gaseous products secured in dealkylating isopropylbenzene is given in Table 2. The results of analysis indicate that no matter what the test conditions were, the bulk of the gaseous products consisted of propylene and propane (90% by volume and higher). Some methane was found in

TABLE 2

Composition of the Gaseous Products Secured in the Dealkylation of Isopropylbenzene Above an Aluminosilicate Catalyst*

Test No.	% by volume										
	H_2	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	iso-C_4H_8	n-C_4H_8	ΣC_4H_{10}	ΣC_nH_{2n}	ΣC_nH_{2n+2}
27	–	–	–	–	57.0	43.0	–	–	–	57.0	43.0
26	–	–	–	–	60.0	40.0	–	–	–	60.0	40.0
23	–	–	–	–	75.0	25.0	–	–	–	75.0	25.0
6	–	4.4	–	–	88.0	7.6	–	–	–	88.0	12.0
7	–										
2	–	2.8	–	–	95.7	1.5	–	–	–	95.7	4.3
3	–	2.5	–	–	93.5	4.0	–	–	–	93.5	6.5
4	–	2.5	–	–	94.0	3.5	–	–	–	94.0	6.0
9	–	2.0	–	–	95.0	3.0	–	–	–	95.0	5.0
10	–										
11	–	1.0	–	–	98.0	1.0	–	–	–	98.0	2.0
16	2.0	2.2	0.4	–	86.5	6.0	–	1.9	1.0	88.8	9.2
17											
18	1.9	3.2	0.3	1.2	88.5	3.2	–	1.1	0.6	89.9	8.2
19											
20	1.7	1.7	0.1	0.1	92.5	2.9	–	0.9	0.1	93.5	4.8
21	0.1	2.5	–	–	93.8	3.1	–	0.5	–	94.3	6.6
22	1.8	2.6	–	–	94.0	1.6	–	–	–	94.0	4.2
24	1.6	2.9	–	–	94.2	1.3	–	–	–	94.2	4.2
14	2.0	6.0	0.2	0.2	84.0	4.5	1.2	1.4	0.5	86.8	11.2
15											
13	1.2	2.0	–	0.1	93.1	2.2	0.3	1.0	0.1	94.4	4.4
12	1.3	1.0	0.5	0.2	94.5	1.9	0.1	0.5	–	95.6	3.1
34	1.1	0.8	0.3	0.3	93.3	2.7	–	1.4	0.1	95.0	3.9
31	2.3	0.8	1.3	–	92.4	1.8	–	1.3	0.1	95.0	2.7
33	0.2	3.9	0.4	0.2	93.3	1.5	–	–	0.5	93.7	6.1
32	–	1.8	–	0.5	93.7	2.0	–	2.0	–	95.7	4.3

*See Table 1 for the experimental conditions.

the gaseous products at 350°. The percentage of methane rose as the contact time was increased (up to 4.4% by volume). The gas secured in the tests run at 400 and 450° contained traces of ethylene, ethane, n-butylenes, butanes, and hydrogen, in addition to methane. At 450° the gaseous product contained as much as 1% of isobutylene. As we see from the last column in Table 2, the gaseous products contained an appreciable percentage of saturated hydrocarbons. The formation of saturated hydrocarbons must be attributed to the hydrogen disproportionation reaction discovered by Mikhnovskaya and Frost [6]. It is worthy of note that the greatest disproportionation of the hydrogen occurred at 300° for a volumetric rate of flow of 0.5 liters per liter of catalyst per hour (ΣC_nH_{2n+2} = 25%). Thomas, Hoekstra, and Pinkston have shown in their paper [2] that the gaseous products secured in the dealkylation of isopropylbenzene at 400 to 500° consisted of propylene, propane, butylenes, and butanes. In our opinion, it is extremely strange that the cited authors found no hydrogen, methane, ethane, or ethylene.

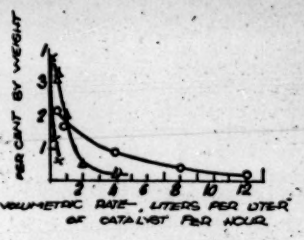

Fig. 1. Variation of the coke yield with the volumetric rate at 300, 350, and 400°.

Notation: X - Temperature 300°; Δ - 350°; 0 - 400°.

In rectifying the liquid products, we collected fractions whose boiling points were those of benzene and isopropylbenzene and a 192-210° fraction. A detailed analysis indicated that the 75-85° fraction consisted almost entirely of benzene, with a trace of unsaturated hydrocarbons (below 1%). The 150-160° fraction consisted of unchanged isopropylbenzene. The 192-210° fraction recovered from the catalyzates produced in the tests run at 350° had the following constants: d_4^{20} 0.8594; n_D^{20} 1.4917; molecular weight 161. These constants are close enough to those given in the literature for diisopropylbenzens [7].

To determine the structure of the di-isopropylbenzenes, we oxidized the 192-210° fraction with nitric acid (1:3). Isophthalic acid and terephthalic acids were found in the oxidation products in the ratio of 1:2 by the method described by Dobryansky and Obolentsev [8]. The m.p. of the isophthalic acid was 345°. The terephthalic acid sublimed at approximately 300°. We prepared the dimethyl esters of the isophthalic and terephthalic acids. The m.p. of the dimethyl isophthalate was 64° after sublimation; the dimethyl terephthalate had a m.p. of 140°. The recovery of isophthalic and terephthalic acids from the oxidation products of the 192-210° fraction is evidence that the fraction contained 1,3- and 1,4-di-isopropylbenzenes in the ratio of 1:2. The presence of meta and paradi-isopropylbenzene in the dealkylation products of isopropylbenzene explains the discrepancy between the yields of propylene and benzene noticed by Moldavsky and Bezdel [1] and also observed in the present research.

We attribute the high percentage of benzene in the catalyzate, which exceeds the theoretical value, and the presence of meta- and paradi-isopropylbenzene to a dismutation of the isopropylbenzene in accordance with the following equation:

$$2C_6H_5C_3H_7 = C_6H_6 + C_6H_4(C_3H_7)_2.$$

A convenient review of the relationships between the principal reaction in the dealkylation of isopropylbenzene and the dismutation side reaction is afforded by the data listed in Table 3. Inspection of this table shows the tendency of the dismutation reaction to gain as the temperature is lowered. At the comparatively low temperatures of 350-400° the extent of the dismutation

TABLE 3

Data on the Conversion of Isopropylbenzene in Accordance with the Equations:

$C_6H_5(C_3H_7) \longrightarrow C_3H_6 + C_6H_6$ (I) and $2C_6H_5(C_3H_7) \longrightarrow C_6H_6 + C_6H_4(C_3H_7)_2$ (II)

Test No.	Temperature	Volumetric rate, liters per liter of catalyst per hour	Per cent conversion, per cent by weight, based on the original product				
			Benzene		Propylene*	Di-isopropylbenzene	Propylene + benzene [cf Equation (I)]
			Total benzene	Formed as the result of dismutation [cf Equation (II)]			
6	350	0.5	20.8	3.0	8.9	6.3	26.7
7	350	0.5	21.0				26.9
2	350	1.0	16.6		6.6	6.9	19.9
3	350	1.0	16.7	3.3	7.3		20.7
4	350	1.0	16.8		6.9	7.0	20.4
9	350	2.0	11.8	2.2	5.5	4.5	15.1
10	350	2.0	11.7		5.8		15.3
11	350	4.0	8.0	1.3	3.8	2.8	10.5
16	400	0.5	35.6	4.2	13.9	8.8	45.3
17	400	0.5			13.1		44.5
19	400	1.0	29.7	2.7	14.0	4.5	41.5
20	400	2.0	29.7	2.0	14.1	4.1	41.8
21	400	4.0	26.4	1.3	12.6	2.7	37.7
22	400	8.0	19.6	2.4	8.8	5.0	26.0
24	400	12.0	13.0	2.5	4.8	5.3	15.3
14	450	0.5	36.0	0.8	16.9	1.8	52.1
15	450	0.5	36.0		17.5		52.7
13	450	1.0	37.4	0.9	18.9	1.9	55.4
12	450	2.0	37.0	0.8	19.1	1.8	55.3
34	450	8.0	33.9	1.5	15.6	3.2	48.0
31	450	10.0	27.1	1.5	13.8	3.1	39.4
33	450	12.0	23.8	1.4	11.9	3.0	34.3
32	450	15.0	17.0	1.7	9.0	3.5	24.3

of isopropyl benzene increases with the length of the contact time. As the temperature is raised to 450°, the curve representing the extent of dismutation as a function of the time of contact should pass through a maximum. In the range we investigated the extent of conversion dropped as the time of contact was increased, which we attribute to an appreciable increase in the secondary dealkylation of di-isopropylbenzene in accordance with the equation suggested by Mamedaliev [4].

If allowance is made for the benzene formed as the result of dismutation, the precentages of benzene and propylene are equal, within the limits of experimental error.

In Test No. 31, for instance, in view of the quantity of propylene and di-isopropylbenzene, the amount of benzene formed should have been 27.1% by weight of the theoretical, based on the original product. We found experimentally that the benzene formed totaled 27.1% by weight. The figures were 23.5% and 23.8% by weight, respectively, in Test No. 33, 16.9% and 17.0% by weight, respectively, in Test No. 32, and so forth.

*Including propane.

Kinetics of the dealkylation of isopropylbenzene. We employed the kinetic equations of Kazeev [1], modified somewhat by us, in the kinetic treatment of our data:

$$\ln \frac{D}{D - M} = a\tau^b, \qquad (1)$$

where D is the maximum dealkylation of the isopropylbenzene (in per cent) at the given temperature; M is the extent of dealkylation of the isopropylbenzene at the given temperature (in per cent); τ is the conventional time of contact; a is a parameter characterizing the reaction rate; and b is a dimensionless parameter characterizing the type of reaction.

$$\omega = (100 - \xi) \cdot a \cdot b \cdot \tau^{b-1}, \qquad (2)$$

where ω is the reaction rate; $\xi = 100\frac{M}{D}$ is the extent of dealkylation of the isopropylbenzene at the time τ, expressed as per cent of the maximum dealkylation at the given temperature.

The values of M for the dealkylation of isopropylbenzene are given in the last column of Table 3. We found the values of D experimentally for the temperatures of 400 and 450°, as indicated earlier. We calculated the value of D for 350° by the method proposed by Kazeev. We did this by plotting a series of anamorphoses of the type $P = D\exp(-a\tau^b)$ (where $P = D - M$) for various values of D and taking the value of D for which the anamorphosis fitted the experimental points most closely (Fig. 2). The results secured by us at 300° were inadequate for deriving kinetic equations.

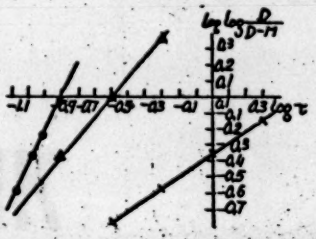

Fig. 2. Variation of $\log \frac{D}{D - M}$ with $\log \tau$.

Notation: X - temperature 350°; Δ - 400°; O - 450°.

At the present time either the reciprocal of the volumetric rate (1/v), or the conventional time of contact τ (cf the paper by Orochko [10]) is used in determining the time the product remains in the reaction zone. For our kinetic calculations we used the reciprocal of the volumetric rate. We also computed the time of contact from the equation [10]

$$\tau = \frac{Q_r \cdot \eta \cdot 273 \cdot 3600}{Q_m \cdot (2 + \alpha) \cdot T_r},$$

where Q_r is the volume of the reaction zone; η is the proportional free volume of the catalyst ($\eta = 0.335$ for an aluminosilicate catalyst [10]); Q_m is the volume of hydrocarbon vapor passing through the reaction zone per hour reduced to standard conditions; α is the extent of conversion; T_r is the temperature of the reaction zone.

Henceforth, unless expressly stated otherwise, the data cited are based on 1/v. At 350, 400, and 450°, the dealkylation of isopropylbenzene is described by Equation (1) with the values of the parameters a, b, and D given in Table 5.

Table 4 gives the calculated and experimental values of M as well as the values of ω for the dealkylation of isopropylbenzene. The curves for ω corresponding to 400 and 450°, exhibit a clearly marked maximum (Fig. 3). The relationship between the $(1/v)_{max}$ (corresponding to the maximum reaction rate)

TABLE 4

Variation of the Extent and Rate of the Dealkylation of Isopropylbenzene With the Temperature and the Volumetric Rate

Test No.	Temperature	$\tau = \frac{1}{v}$	log τ	log log $\frac{D}{D-m}$	Extent of dealkylation of the isopropylbenzene		Rate of dealkylation of the isopropylbenzene, ω
					$M_{exp.}$	$M_{calc.}$	
6	350°	2.00	0.301	-0.143	26.7	26.7	11.3
7	350	2.00	0.301	-0.135	26.9		10.8
2	350	1.00	0	-0.395	19.9		28.5
3	350	1.00	0	-0.365	20.7	21.1	26.6
4	350	1.00	0	-0.380	20.4		27.4
9	350	0.50	-0.301	-0.570	15.1	15.5	48.8
10	350	0.50	-0.301	-0.570	15.3		49.3
11	350	0.25	-0.602	-0.775	10.5	10.5	73.8
20	400	0.50	-0.301	+0.365	41.8	41.8	6.5
21	400	0.25	-0.602	-0.004	37.4	37.6	115
22	400	0.125	-0.904	-0.376	26.0	26.0	359
24	400	0.083	-1.079	-0.699	15.3	18.3	450
34	450	0.125	-0.904	-0.020	48.0	48.0	405
31	450	0.100	-1.000	-0.245	39.4	40.5	778
33	450	0.083	-1.079	-0.360	34.3	33.1	863
32	450	0.067	-1.176	-0.586	24.3	24.3	1023

TABLE 5

Kinetic Data on the Catalytic Dealkylation of Isopropylbenzene

Test No.	Temperature	D	b		a		$\left(\frac{1}{v}\right)_{max}$	ω_{max}	ξ_{max}	M_{max}
			for $1/v$	for τ	for $1/v$	for τ				
6, 3, 10, 11	350°	33	0.703	0.725	1.02	0.463	-	-	-	-
20, 21, 22, 24	400	42	1.235	1.295	12.5	4.0	0.034	577	17.1	7.2
34, 31, 32, 33	450	56	2.08	2.38	167	40.4	0.0625	1033	40.5	21.9

and the kinetic parameters is given by the equation:

$$\left(\frac{1}{v}\right)_{max} = \left(\frac{b-1}{ab}\right)^{1/b}.$$

This equation was used to find the values of $\left(\frac{1}{v}\right)_{max}$. The values of $\left(\frac{1}{v}\right)_{max}$, ω_{max}, ξ_{max}, and M_{max} are listed in Table 5.

At 350° the value of the parameter b, 0.703, indicates that the order of the reaction is close to that of a bimolecular reaction ($b \cong 0.63$ for a bimolecular reaction). At 400 and 450°, $b > 1$, evidence of the existence of an induction period. The change in the kinetic parameter b as the temperature rises indicates that the dealkylation of isopropylbenzene cannot be described by any one equation of a discrete order of reaction. It must be assumed that the mechanism of the reaction involved in the dealkylation of isopropylbenzene varies with the temperature. The variation of the kinetic parameters a and b is described by equations of the general type:

$$a = A \cdot e^{\frac{-Q_a}{RT}}, \quad b = B \cdot e^{\frac{\pm Q_b}{RT}},$$

where A is the catalytic coefficient, B is the activity coefficient, Q_a is the kinetic volume energy, and Q_b is the kinetic surface energy.

In our instance, the parameters a and b are expressed by the equations:

$$a = 376 \cdot 10^{11} \cdot e^{\frac{-39589}{RT}} \quad \text{and} \quad b = 3685 \cdot e^{\frac{-10530}{RT}}.$$

The conventional time of contact was employed in deriving these equations. The kinetic indexes of the dealkylation process, as computed with $1/v$ and τ, are given in Table 5 for the sake of comparison. We see that the parameter b varies somewhat with the method used to compute the time of contact, whereas the parameter a, which has the dimension of time, is wholly governed by the method used for this computation.

The high value of Q_a = -39590 cal/mole, and the variation of the parameter b with temperature are evidence of the markedly heterogenous nature of this reaction. Further research is required to elucidate the nature of the autocatalytic aspects of the reaction involved in the dealkylation of isopropyl benzene.

SUMMARY

1. The kinetics of the reaction involved in the dealkylation of isopropylbenzene above an aluminosilicate catalyst at temperatures ranging from 350 to 450° have been described.

2. It has been found that the principal reaction in the dealkylation of isopropylbenzene is accompanied by the dismutation of the isopropylbenzene as follows:

$$C_6H_5C_3H_7 = C_6H_6 + C_6H_4(C_3H_7)_2.$$

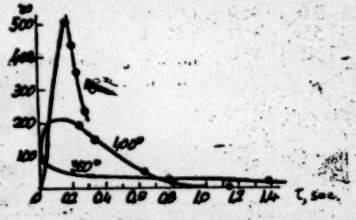

Fig. 3. Variation of rate of dealkylation of isopropylbenzene with τ at temperatures of 350, 400, and 450°.

LITERATURE CITED

[1] B.L.Moldavsky and L.S.Bezdel, J.Gen.Chem. 16, 1633 (1946).
[2] C.L.Thomas, J. Hoekstra, and J.T.Pinkston, J.Am.Chem.Soc. 66 1694 (1944).
[3] B.S.Greensfelder and H.H.Voge, Ind.Eng.Chem., 12, 1168 (1945).
[4] Yu.G.Mamedaliev, Bull. USSR Acad. Sci., Div. Chem.Sci., 1947, 197.
[5] P.D.Obolentsev, J.Appl.Chem., 22, 9 (1949).
[6] A.A.Mikhnovskaya and A.V.Frost, Proc. Acad. Sci., USSR, 37, 252 (1942).
[7] P.D.Obolentsev. The Physical Constants of the Constituents of Light Motor Fuels. State Fuel Press. (1943).
[8] A.F.Dobryansky and P.D.Obolentsev, J.Gen.Chem. 12, 1810 (1942).
[9] S.A.Kazeev. The Kinetic Principles of Metallurgical Processes. Leningrad (1946).
[10] D.I.Orochko. Kinetic Calculations of Circulation Reaction Equipment for the Synthesis of Liquid Fuel. State Fuel Press, (1947).
[11] E.K.Mankash, G.P.Borisova, D.I.Orochko, and A.V.Frost, Oil Economy, 1946, No. 6-7, 26.
[12] K.V.Topchieva and G.M.Panchenkov, Bull. Moscow State Univ., 1948, No. 11, 133; Proc. Acad.Sci. USSR, 74, 1113 (1950).

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THE CYCLOALKYLATION OF AROMATIC COMPOUNDS

IV. CONDENSATION OF 1-METHYLCYCLOHEXANOL-1 WITH BENZENE, TOLUENE AND PHENOL

N. G. Sidorova

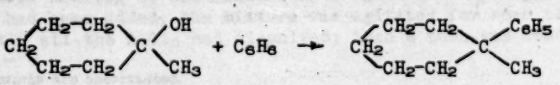
When aromatic compounds are alkylated with cyclic compounds in the presence of aluminum chloride, more types of isomerization may occur than when aliphatic substances are employed. Besides the isomerization due to the migration of hydrogen that generally accompanies alkylation, transformations may take place in which the number of carbon atoms in the ring is changed, as well as cis-trans rearrangements. With the reaction able to take many different courses, it is obvious that identification of the products is a complicated affair.

The chemical nature of the substances used for alkylation may affect the degree and direction of the isomerization. In our previous research [1], on the cycloalkylation of aromatic hydrocarbons with alcohols, for instance, it was shown that optically active alcohols give rise to products that possess perceptible, even if slight, rotatory power. This is evidence that at least some of the substances was formed in a direct exchange reaction without isomerization. Further evidence of this is the discovery of 1-methyl-2-phenylcyclohexane among the products of the alkylation of benzene by 1-methylcyclohexanol-2. This indicates that isomerization is not complete in alkylation by alcohols under conditions where nothing but an isomerized product is recovered from halogen derivatives.

On the other hand, however, alkylation by alcohols may yield products of more thoroughgoing isomerization, involving the shift of a hydrogen atom to a more distant carbon atom rather than to the adjacent one. The probability of such a reaction in the case of cyclic alcohols is borne out by the work of Wallach [2], who has shown that the dehydration of 1,3- and 1,4-methylcyclohexanols with zinc chloride yields 1-methylcyclohexene-1, in addition to other products.

We have begun an investigation of the cycloalkylation of aromatic compounds with $AlCl_3$, using the simplest compounds, in order to elucidate the directions taken by these isomerizations. We used benzene and the isomeric methylcyclohexanols. The present paper reports on the results of the condensation of 1-methylcyclohexanol-1 with benzene in the presence of $AlCl_3$. In passing, we made a study of the reaction of 1-methylcyclohexanol-1 with phenol in the presence of H_3PO_4.

Only one type of isomerization is possible with 1-methylcyclohexanol-1: a change in the size of the ring. But isomerization of this sort is negligible in six-membered rings, so that we may be certain of the structure of the principal reaction product:



The reaction of 1-methylcyclohexanol-1 with benzene requires less $AlCl_3$ than condensation of secondary cyclic alcohols. The reaction occurs with as little as 0.5 gram-equiv. of $AlCl_3$. The yield of the monoalkylated product totaled some 50% of the theoretical, that of the dialkylated product being about 15%.

The monoalkylated product, 1-methyl-1-phenylcyclohexane, was identified by the synthesis of a large number of its derivatives. A number of p-derivatives were prepared from the amine formed by reducing the nitration product of the hydrocarbon. Another series of derivatives was synthesized via the sulfochloride of the hydrocarbon. The ortho and para isomers were formed in this series. Separation of these isomers entailed considerable difficulty in most instances, owing to the slight difference in their solubilities and the similarity of their crystalline structures. An exception was the sulfotoluidide, the isomers of which could be readily separated by mechanically selecting the crystals, whose forms differed very much.

When we tried to secure a dinitro compound by nitrating the mononitro product, we secured a high percentage of m-dinitrobenzene, formed as the result of the substitution of a nitro group for the radical. Instances of such splitting off of the alkyl group are not unknown: it sometimes takes place even during the synthesis of the mononitro product, the heavier and more highly branched radical being split off [3].

The transformation products of 1-methyl-1-phenylcyclohexane included a phenol, which was subsequently recovered in the condensation of phenol with 1-methylcyclohexanol-1 in the presence of H_3PO_4. This condensation was carried out by the method developed by Tambovtseva and Tsukervanik [4]. The reaction yielded a cycloalkylphenol and the corresponding phenol ether. Distillation of the latter caused its total conversion into an alkylphenol. The total yield of the latter was 79% of the theoretical. The identity of this product with the phenol formed from 1-methyl-1-phenylcyclohexane indicates that this compound is p-(1-methylcyclohexyl)-phenol. All of our efforts to isolate the ortho isomer met with failure. Apparently, it is either not formed at all or only in negligible quantities.

No detailed study was made of the heavy fraction recovered in the alkylation of the benzene. It is probably a mixture of m- and p-di(1-methylcyclohexyl)-benzenes, inasmuch as its oxidation by dilute nitric acid yielded a mixture of isophthalic and terephthalic acids, which were identified via their methyl esters.

We also condensed toluene with 1-methylcyclohexanol-1, but we made no detailed analysis of the reaction products.

All the substances we have synthesized are new ones, not hitherto described in the literature.

EXPERIMENTAL *

1-Methylcyclohexanol-1 was prepared by a Grignard reaction from cyclohexanone and CH_3MgI [5]. The yield was 60%. B.p. 150-153° (727 mm).

Condensation of 1-methylcyclohexanol-1 with benzene. We used 5.7 g (0.05 mole) of 1-methylcyclohexanol-1, 3.3 g (0.025 mole) of $AlCl_3$, and 40 ml (0.4 mole) of benzene. The finely pulverized $AlCl_3$ was slowly added in small batches, with constant stirring, to the alcohol-benzene mixture in a flask fitted with a reflux condenser terminated by a calcium chloride tube, at such a rate as to prevent any perceptible heating of the mixture or evolution of hydrogen chloride. After all the $AlCl_3$ had been added, the mixture was agitated for some time at room temperature until all the $AlCl_3$ had dissolved; then a tube was connected to

* All boiling and melting points are uncorrected.

the end of the condenser to lead off the hydrogen chloride, and the mixture was heated over a warm water bath. As the evolution of the HCl diminished, the bath temperature was raised, the contents of the flask being heated to a boil toward the close and the boiling being continued until no more HCl was evolved. After the reaction mixture had cooled, it was treated with cold acidulated water, and the benzene layer was removed, washed with water until its reaction was neutral, desiccated with calcium chloride, and fractionated above metallic sodium.

This yielded 4.4 g (50% of the theoretical) of a monoalkylated product (1-methyl-1-phenylcyclohexane) with a b.p. of 128° (20 mm) and 1.5 g (15% of the theoretical) of a dialkylated product with a b.p. of 215-220° (20 mm).

1-Methyl-1-phenylcyclohexane. This is a colorless liquid with a pleasant odor.

B.p. 75° (2 mm); 93° (5 mm); 128° (20 mm); 133° (30 mm); d_4^{17} 0.9388; n_D^{17} 1.5233; MR_D 56.69; Computed 56.43.

0.1141 g substance: 0.3747 g CO_2; 0.1094 g H_2O. Found %: C 89.56; H 10.65. $C_{13}H_{18}$. Computed %: C 89.65; H 10.35.

4-(1-Methylcyclohexyl)-nitrobenzene. 50 ml of a mixture of equal volumes of HNO_3 (d 1.4) and H_2SO_4 (d 1.84), were added in small batches, with constant shaking and chilling with water to 10 g of 1-methyl-1-phenylcyclohexane. Then the mixture was heated over a warm water bath for approximately 30 minutes. The cooled mixture was poured out over ice and extracted with ether; the ether extract was washed repeatedly with water, desiccated, and fractionated. The yield of the nitro compound was 10.1 g (80% of the theoretical).

B.p. 145-150° (3 mm); d_4^{16} 1.1073; n_D^{16} 1.5530; MR_D 63.32; computed 62.63.

5.24 mg substance: 0.308 ml N_2 (25°, 701 mm). Found %: N 6.21. $C_{13}H_{17}O_2N$ Computed %: N 6.39.

Oxidation with dilute HNO_3 (15%) at 140-150° in a sealed tube yielded p-nitrobenzoic acid, which fused at 235-237° with slight decomposition after one recrystallization from alcohol.

Nitration of 4-(1-methylcyclohexyl)-nitrobenzene. 1 g of the nitro compound was treated with 3 ml of equal volumes of HNO_3 (d 1.52) and H_2SO_4 (d 1.84). At the beginning the mixture was chilled with ice water, but thereafter it was agitated for 0.5 hour at room temperature and finally heated for about 0.5 hour over a warm water bath. The reaction product was recovered in the usual manner. Part of the mixture crystallized during the evaporation of the ether. The isolated crystals had a constant m.p. of 89° after their first crystallization (from dilute alcohol or petroleum ether). A test sample, mixed with m-dinitrobenzene, fused at 89°.

3.57 mg substance: 0.561 ml N_2 (25°, 709 mm). Found %: N 16.78. $C_6H_4O_4N_2$. Computed %: N 16.67.

The liquid portion of the nitration product was not analyzed.

4-(1-Methylcyclohexyl)-aniline. 7 g of the mononitro compound was reduced in the customary manner with tin and hydrochloric acid. After the reaction was over, steam was passed through the acid solution to remove possible traces of the nitro compound. Then an excess of alkali was added to the reaction mixture, and the amino compound was distilled with steam. The amine was extracted from the distillate with benzene, desiccated with KOH, and distilled in vacuum after the benzene had been driven off. This yielded 5.3 g (88% of the theoretical).

B.p. 129-130° (3 mm); d_4^{20} 1.0040; n_D^{20} 1.5607; MR_D 60.98; Computed 59.85.

A light yellow oil; darkens rapidly and decomposes upon standing.

Acetamino derivative. M.p. 147-148° (from benzene).

4.43 mg substance: 0.272 ml N_2 (25°, 702 mm). Found %: N 6.49. $C_5H_{11}ON$. Computed %: N 6.06.

Benzamino derivative. M.p. 236° (from dilute alcohol).

3.67 mg substance: 0.178 ml N_2 (25°, 702 mm). Found %: N 5.13. $C_{20}H_{23}ON$. Computed %: N 4.78.

p-Nitrobenzamino derivative. M.p. 203-204° (from a benzene-petroleum ether mixture).

4.90 mg substance: 0.390 ml N_2 (25°, 702 mm). 4.13 mg substance: 0.338 ml N_2 (25°, 703 mm). Found %: N 8.42, 8.67. $C_{20}H_{22}O_3N_2$. Computed %: N 8.28.

Picrate. M.p. 186° (from benzene). Minute, bright-yellow needles.

5.67 mg substance: 0.664 ml N_4 (13°, 720 mm); 5.10 mg substance: 0.627 ml N_2 (22°, 711 mm). Found %: N 13.25, 13.31. $C_{18}H_{22}O_7N_4$. Computed %: N 13.40.

4-(1-Methylcyclohexyl)-phenol. The amine was diazotized with a calculated quantity of sodium nitrite in hydrochloric acid. The diazo compound colored the solution yellow when it was combined with β-naphthol in an alkaline medium. When the diazo compound was heated over a water bath, it decomposed violently, evolving nitrogen, the solution becoming intensely colored. The reaction product was distilled with steam, the phenol being extracted from the distillate with benzene, desiccated with calcium chloride, and fractionated at 130-150° (6 mm) after the solvent had been driven off. A reddish substance was distilled, which quickly crystallized. The crystals were squeezed out on a porous plate and recrystallized from petroleum ether, after which they had a m.p. of 105°. Small, elongated, snow-white needles.

(1-Methylcyclohexyl)-benzene sulfochloride [6]. 8 ml of chlorosulfonic acid was gradually added at room temperature to 6.2 g of 1-methyl-1-phenylcyclohexane dissolved in 20 ml of carbon tetrachloride. The mixture was agitated at room temperature for 30 minutes, and then it was poured out over ice. Carbon tetrachloride was added to the mixture until all the sulfochloride had been dissolved, and the solution was separated, washed with dilute KOH, and then with water, desiccated with calcium chloride, and distilled. The sulfochloride distilled at 165-169° (2 mm) as a cloudy liquid.

(1-Methylcyclohexyl)-benzenesulfamide. This was prepared by heating the the sulfochloride with an excess of ammonium carbonate over a water bath. After the reaction was complete, water was added to the mixture, and the precipitate was filtered. Repeated recrystallization from dilute alcohol or petroleum ether yielded the pure para isomer of the sulfamide as white needles with a m.p. of 117°.

4.09 mg substance: 0.224 ml N_2 (25°, 704 mm). Found %: N 5.81. $C_{12}H_{19}O_2SN$. Computed %: N 5.53.

Crystals with a m.p. of 90° were recovered from the mother liquor. They are evidently the ortho isomer of the sulfamide, but there is not certainty as to their individuality.

(1-Methylcyclohexyl)-benzenesulfoanilide. This was synthesized by agitating an excess of aniline with a benzene solution of the sulfochloride. The reaction was accompanied by the evolution of heat; toward the close the mixture

was heated for a few minutes over a water bath. The benzene solution was washed with dilute hydrochloric acid and then with water, and desiccated with $CaCl_2$. Evaporation of the benzene left a thick, sticky mass, part of which crystallized after a few days had elapsed. We were unable to isolate and purify these crystals, however, inasmuch as they softened under the slightest stress.

(1-Methoxycyclohexyl)-benzenesulfo-p-toluide. This was analogously synthesized from the p-toluide and the sulfochloride. Two different kinds of crystals were clearly visible during crystallization: minute needles and prisms. It was easy to isolate the ortho and para isomers in the pure state by separating these crystals mechanically and then recrystallizing them. The slightly soluble crystals, evidently the para isomer, had a m.p. of 114-115° (from petroleum ether or dilute alcohol). They crystallized as needles.

10.74 mg substance: 0.447 ml N_2 (22°, 714 mm). Found %: N 4.52.
$C_{20}H_{25}SO_2N$. Computed %: N 4.08.

The second product, apparently the ortho isomer, fused at 103-104° (from petroleum ether or dilute alcohol). Prisms.

4.11 mg substance: 0.165 ml N_2 (23°, 714 mm): Found %: N 4.35.
$C_{20}H_{25}SO_2N$. Computed %: N 4.08.

(1-Methylcyclohexyl)-benzosulfonic acid. This was synthesized as its sodium salt by hydrolyzing the sulfochloride with a 10% NaOH solution. The salt was recrystallized from water. It was isolated as small flakes.

0.5067 g substance: 0.0308 g H_2O. Found %: H_2O 6.08.
$C_{13}H_{17}SO_3Na \cdot H_2O$. Computed %: H_2O 6.12.

The barium salt was prepared by precipitating a solution of the sodium salt with $BaCl_2$. Two kinds of crystals were clearly visible when the salt was crystallized from water (evidently the ortho and para isomers). The slightly soluble portion settled out as small flakes, while the more soluble crystals settled out as small needles. We analyzed the first crystal fraction.

0.0658 g substance: 0.0035 g H_2O; 0.0226 g $BaSO_4$. Found %: H_2O 5.32; Ba 20.21. $(C_{13}H_{17}SO_3)_2Ba \cdot 2H_2O$. Computed %: H_2O 5.30; Ba 20.21.

The 215-220° (20 mm) fraction, secured in the condensation of benzene with 1-methylcyclohexanol-1, had the following constants:

d_4^{17} 0.9775; n_D^{17} 1.5400; MR_D 86.74; computed 86.57.

0.1174 g substance: 0.3830 g CO_2; 0.1146 g H_2O. Found %: C 88.97; H 10.84. $C_{20}H_{30}$. Computed %: C 88.89; H 11.11.

Oxidation by dilute HNO_3 (15%) at 150° in a sealed tube yielded a mixture of acids, which was esterified with diazomethane. The resultant methyl esters were separated by crystallization from alcohol. We secured the dimethyl ester of terephthalic acid, with a m.p. of 139°, and the dimethyl ester of isophthalic acid, with a m.p. of 63°.

Condensation of toluene with 1-methylcyclohexanol-1. We used 5.7 g (0.05 mole) of 1-methylcyclohexanol-1, 3.3 g (0.025 mole) of $AlCl_3$, and 40 ml of toluene for the reaction.

The reaction conditions were the same as those for benzene.

We secured 14.4 g (47% of the theoretical of (1-methylcyclohexyl)-toluene (a mixture of the ortho and para isomers).

B.p. 127° (9 mm); d_4^{26} 0.9271; n_D^{26} 1.5164; MR_D 61.34. Computed 61.05.

0.1328 g substance: 0.4342 g CO_2; 0.1253 g H_2O. Found %: C 89.17; H 10.49. $C_{14}H_{20}O$. Computed %: C 89.36; H 10.64.

Condensation of phenol with 1-methylcyclohexanol-1. We used 7.4 g (0.065 mole) of 1-methylcyclohexanol-1, 8.0 g (0.085 mole) of phenol, and 30 ml of H_3PO_4 (d 1.86), for the reaction.

This reaction was carried out in a round-bottomed two-necked flask, fitted with a reflux condenser and a mechanical stirrer. The reagents were added in a single bath, and the reaction mixture was heated to 100-120° (temperature of the mixture) for 3 hours, with mechanical stirring. After the reaction was complete ether and water were added to the mixture; the acid layer was separated, and the ether extract was washed with water. The phenol was separated from the phenol ether by reagitating the ether solution of the reaction products with a 10% KOH solution. The phenol was recovered from the alkaline solution by acidifying the latter. The further purification followed the usual lines.

4(-1-Methylcyclohexyl)-phenol [7] was secured by distilling the phenolic portion. B.p. 159-162° (11 mm). Yield: 7.5 g (61% of the theoretical). The colorless liquid crystallized when chilled. A phenol with a m.p. of 108° was likewise recovered from the ether portion by distilling the latter. Yield: 2.2 g (18% of the theoretical).

The total yield of the 4-(1-methylcyclohexyl)-phenol was 79%. A test sample mixed with the 4-(1-methylcyclohexyl)-phenol synthesized from 1-methyl-1-phenylcyclohexane, exhibited no depression of the melting point.

The phenol turned an alcoholic solution of $FeCl_3$ green.

0.0660 g substance: 0.1986 g CO_2; 0.0574 g H_2O. Found %: C 82.07; H 9.66. $C_{13}H_{18}O$. Computed %: C 82.11; H 9.47.

Acetic ester: b.p. 170-172° (13 mm).

d_4^{20} 1.0427; n_D^{20} 1.5258; MR_D 68.32; computed 67.32.

0.0880 g substance: 0.2506 g CO_2; 0.0712 g H_2O. Found %: C 77.64; H 8.99. $C_{15}H_{20}O_2$. Computed %: C 77.59; H 8.62.

Benzoic ester: m.p. 80-81° (from dilute alcohol).

0.0822 g substance: 0.2454 g CO_2; 0.0580 g H_2O. Found %: C 81.42; H 7.84. $C_{20}H_{22}O_2$. Computed %: C 81.63; H 7.48.

p-Nitrobenzoic ester: m.p. 143° (from alcohol).

9.36 mg substance: 0.394 ml N_2 (24°, 713 mm). Found %: N 4.53. $C_{20}H_{21}O_4N$. Computed %: N 4.13.

SUMMARY

1. A study has been made of the condensation of methylcyclohexanol-1 with benzene and toluene in the presence of $AlCl_3$. The condensation product with benzene: 1-methyl-1-phenylcyclohexane, was identified by preparing a series of its derivatives.

2. A study has been made of the condensation of 1-methylcyclohexanol-1 with phenol in the presence of H_3PO_4. This condensation yielded 61% of p-(1-methylcyclohexyl)-phenol and 18% of a 1-methylcyclohexyl ether of the phenol. Distillation of the latter caused its complete isomerization into p-(1-methylcyclohexyl)-phenol, which was identified by preparing several of its derivatives.

3. It has been proved that the p-(1-methylcyclohexyl)-phenol produced by the alkylation of phenol is the same as the product of the diazotization of p-(1-methylcyclohexyl)-aniline.

LITERATURE CITED

[1] I.P.Tsukervanik and N.G.Sidorova, J.Gen.Chem. 8, 1899 (1938).

[2] O.Wallach, Ann., 329, 369 (1903); 359, 306 (1908).

[3] T.Doumania, K.Kobe, Chem. Abs., 36, 1913 (1942).

[4] B.D.Tambovtseva and I.P.Tsukervanik, J.Gen.Chem. 15, 820 (1945).

[5] N.D.Zelinsky, Selected Works, Vol. I, 394 (1941).

[6] A.Newton, J.Am.Chem.Soc., 65, 2439 (1943).

[7] W.Schrauth and K.Quasebarth, Ber., 57, 857 (1924).

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THE KINETICS AND REACTION MECHANISMS OF CATALYTIC HYDRO-DEHYDROGENATION

V. THE CATALYTIC TRANSFORMATIONS OF CYCLOHEXENE IN THE PRESENCE OF COPPER AND IRON

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In the course of our investigation of the reasons for the inertness of copper and iron in the hydrogenation of benzene and the dehydrogenation of cyclohexane, we considered it advisable to make a study of the catalytic transformations of one of the intermediate products of these reactions – cyclohexene – in the presence of these metals.

As we know, cyclohexene may undergo the following transformations: a) hydrogenation to cyclohexene; b) dehydrogenation to benzene; c) redistribution of the hydrogen (disproportionation), benzene and cyclohexane being formed; and d) isomerization to cyclopentene. Many authors have hydrogenated cyclohexene in order to compare the velocity of this process with that of the hydrogenation of benzene. The researches of Lozovoi and Dyakova [1] and Truffault [2] come under this heading. Aside from researches on the hydrogenation of cyclohexene with catalysts that are ordinarily used to hydrogenate benzene – nickel [3], platinum [4], and molybdenum sulfide [5] – there is only one paper describing the hydrogenation of cyclohexene to cyclohexane with a copper catalyst. Sigeru Tutumi [6] has shown that cyclohexene is hydrogenated with a yield of 82% at 170°, above a Cu – Al_2O_3 catalyst. The dehydrogenation of cyclohexene has been studied by Zelinsky and Pavlov [7], using a palladium catalyst; they found that the dehydrogenation of cyclohexene is accompanied by a redistribution of the hydrogen. Zelinksy subsequently investigated, together with Arbuzov [8], the behavior of cyclohexene above various metallic oxides. These researches indicated that at 450° chromic oxide, thorium dioxide, zirconium dioxide, vanadium trioxide, and manganous oxide dehydrogenate cyclohexene to benzene – appreciably in the case of chromic oxide and slightly with the other oxides investigated. At 350-450°, titanium oxide exerts a double effect upon cyclohexene: it isomerizes cyclohexene to methylcyclopentene and dehydrogenates it to benzene. Goldwasser and Taylor [11] made a study of the dehydrogenation of cyclohexene with chromic oxide, finding that cyclohexene is completely dehydrogenated at 510 and 395°, whereas at lower temperatures the principal reaction involved is a redistribution of the hydrogen in the cyclohexene.

Zelinsky made a study of the redistribution of hydrogen in cyclohexene with palladium or platinum [9] and called it an "irreversible catalysis". Several authors have demonstrated that nickel is another catalyst of this reaction [10], both at ordinary and at high pressures. Goldwasser and Taylor [11] have shown that part of the cyclohexene undergoes irreversible catalysis at 276° (31.2% conversion) in the presence of chromic oxide; the percentage conversion of the cyclohexene rises at higher temperatures, at 337° part of the cyclohexene being

dehydrogenated. A.D.Petrov [12] has reported on the partial transformation of cyclohexene in an irreversible catalysis at high pressure and 400-440° with alumina. According to Plate [13], cyclohexene remains unchanged in the presence of alumina at atmospheric pressure and temperatures of 400 to 500°. Plate also investigated the behavior of cyclohexene at 450-500° in the presence of V_2O_3 – Al_2O_3 catalyst, showing that under these conditions cyclohexene undergoes all sorts of transformations. Shcheglova and Kagan [14] have made a study of the kinetics of the disproportionation of hydrogen in cyclohexene in the gas phase with platinized pumice.

The references cited above show that the hydrogen in cyclohexene is redistributed in the presence of catalysts that can hydrogenate benzene and dehydrogenate cyclohexane. It is also asserted in the literature that cyclohexane undergoes irreversible catalysis above iron, as well, though we know that iron does not hydrogenate benzene [15]. In their investigation of the transformations of cyclohexene in the presence of a nickel catalyst, Corson and Ipatiev [10] discovered that the iron walls of the autoclave catalyzed the disproportionation of the hydrogen in cyclohexene (400°).

The isomerization of cyclohexene by metallic oxides was investigated by Zelinsky and Arbuzov [8], who found that alumina, beryllium oxide, and silica gel cause the nearly complete conversion of cyclohexene into methylcyclopentane at 450°. This reaction was also observed by Inoue [16] when he passed cyclohexene above Japanese acid soil at 330°.

We have made a study of the transformations of cyclohexene in the presence of copper and iron catalysts and have investigated the effect of the contact conditions upon these transformations. Depending upon the contact conditions, i.e., the contact temperature, the time of contact, and the extent of dilution with hydrogen or nitrogen, the cyclohexene may, in the presence of copper or iron catalysts, be: a) hydrogenated completely; b) partially hydrogenated and partially disproportionated; c) wholly transformed in a hydrogen disproportionation; and d) partially dehydrogenated and partially disproportionated. At the same time, we have found that neither the hydrogenation of benzene nor the dehydrogenation of cyclohexane takes place in the presence of these copper and iron catalysts under the usual conditions for these latter processes.

Thermodynamic Analysis of the Transformations of Cyclohexene

We have calculated the equilibrium for each of the three reactions: the hydrogenation of cyclohexene, its dehydrogenation, and its disproportionation (hydrogen redistribution) – to ascertain the thermodynamic probability of the conversion of cyclohexene along each of these lines in the temperature range under discussion: 400-600° K.

In our calculations we used the values of the heats of hydrogenation of benzene, cyclohexadiene, and cyclohexene obtained by Kistiakowsky [17] and the heat capacities given by Stull [18]. The heat capacities of benzene, cyclohexane and cyclohexene given by Stull agree with the figures given by Pitzer and Scott for benzene [19] and by Spitzer and Pitzer [20] for cyclohexane, but differ somewhat from the values of the heat capacity of benzene, recently obtained by Scott and his co-workers [21]. An equation for the heat capacity of benzene as a function of the temperature has been derived by Vvedensky [22]. The heat capacities of the hydrocarbons in question were also computed from the spectroscopic data of Stull and Mayfield [23]. We used Stull's data to compute the following values of the heat capacity as a function of temperature: $C_p = 4.19 + 0.055\ T$ for benzene; $C_p = 4.64 + 0.0812\ T$ for cyclohexene; and $C_p = 4.52 + 0.073\ T$ for cyclohexane.

a) Equilibrium of the reaction involving the hydrogenation of cyclohexene: $C_6H_{10} + H_2 = C_6H_{12}$. Using the following value for the heat of hydrogenation of cyclohexene at 355°: $\Delta H_{355} = -28{,}600$ cal [17] and the equation for the heat capacities of the reagents, we got the following equation expressing the variation of the ΔH of the hydrogenation reaction with temperature:

$$\Delta H = -26{,}800 - 6.38\,T + 0.0036\,T^2. \qquad (1)$$

We made use of the following values of the entropy and heat of formation (Cal) of the reaction constituents at 298° K to compute ΔF°_{298} (Table 1).

TABLE 1

	C_6H_{10}	H_2	C_6H_{12}
$\Delta \bar{H}_{298}$ ...	-1.2	0	-29.38
S_{298}	69.18	31.207	71.41

ΔH_{298} for cyclohexene was taken from Frost's figures [24]. The entropy of cyclohexene was calculated from the entropies of benzene and cyclohexane, on the assumption that the entropy increases uniformly during the transitions: $C_6H_6 \rightarrow C_6H_8 \rightarrow C_6H_{10} \rightarrow C_6H_{12}$.

From the data in Table 1 we calculated $\Delta F^\circ_{298} = -28{,}180$ cal. With this value and the value of ΔH given by Equation (1) we derived the following equation, expressing the variation of ΔF° with temperature in the 300-600° K range:

$$\Delta F^\circ = -26{,}800 + 6.38T \ln T - 0.0037\,T^2 - 10.85\,T. \qquad (2)$$

The values of ΔF° calculated from this equation for various temperatures, as well as the values of log K derived from the equation $\log K = -\frac{\Delta F^\circ}{2.3\,RT}$, are listed in Table 2.

TABLE 2

T°	ΔF°	log K
400	-16,464	9.0066
500	-13,298	5.8197
523	-12,620	5.2801
600	-10,024	3.6557

We see that the equilibrium of the equation $C_6H_{10} + H_2 = C_6H_{12}$ is shifted entirely to the right in the 400-600° K range.

b) Equilibrium of the reaction involving the redistribution of the hydrogen in the cyclohexene: $3C_6H_{10} = 2C_6H_{12} + C_6H_6$. The heat evolved in this reaction was calculated from Kistiakowsky's data [17] on the hydrogenation of benzene and cyclohexene: $\Delta H_{355} = 12{,}000$ cal. With this value and the derived equations for the heat capacities, we obtained the following expression for ΔH° in the 300-600° K range:

$$\Delta H = -35{,}842 - 0.09T - 0.0001\,T^2. \qquad (3)$$

Inasmuch as the entropy of three moles of cyclohexene is equal to the sum of the entropies of one mole of C_6H_6 and two moles of cyclohexane in the reaction involving the redistribution of the cyclohexene hydrogen (vide infra), i.e., $\Delta S = 0$, in this particular instance we get:

$$\Delta F^\circ = \Delta H.$$

TABLE 3

T° K	F°	log K
400	-12,012	6.5711
500	-12,046	5.2718
523	-12,054	5.0433
600	-12,085	4.4074

The values of ΔF° and of log K are given in Table 3 for various temperatures.

The data presented in Table 3 are calculated on one mole of cyclohexene. The results of the calculations show that in the given

temperature interval the equilibrium as a whole is shifted in the direction of formation of cyclohexane and benzene.

c) Equilibrium of the reaction involving the dehydrogenation of cyclohexene to benzene: $C_6H_{10} = C_6H_6 + 2H_2$. Let us denote the standard free energy change in the hydrogenation of cyclohexene by ΔF_1°, in the reaction involved in the redistribution of the hydrogen in the three molecules of cyclohexene, $3C_6H_{10} = C_6H_6 + 2C_6H_{12}$, by $3\Delta F_2^\circ$, and the free energy change in the dehydrogenation of cyclohexene by ΔF°. Since free energies are additive, we get:

$$\Delta F^\circ = 2\Delta F_1^\circ - 3\Delta F_2^\circ \ldots$$

The numerical values of ΔF° obtained in this manner are tabulated in Table 4.

TABLE 4

T° K	ΔK°	log K
400	-3,110	1.7013
500	-9,541	4.1755
523	-10,923	4.1519
600	-16,208	5.9110

The values of ΔF° for the specified transformations of cyclohexene are listed in Table 5 for the 400-600° K range.

TABLE 5

Free Energy Changes in Various Transformations of Cyclohexene

Reaction	ΔF_{400}°	ΔF_{500}°	ΔF_{523}°	ΔF_{600}°
$C_6H_{10} + H_2 = C_6H_{12}$	-16,464	-13,298	-12,620	-10,024
$C_6H_{10} = \frac{1}{3} C_6H_6 + \frac{2}{3} C_6H_{12}$	-12,012	-12,046	-12,054	-12,085
$C_6H_{10} = C_6H_6 + 2H_2$	- 3,110	- 9,541	-10,923	-16,208

We may conclude from the data in Table 5 that all three of the conversions of cyclohexene are thermodynamically probable at the temperatures involved in our investigation (400-600° K), changes in temperature affecting the free energy change of each transformation differently. Though the free energy of the disproportionation reaction varies but little with temperature, the hydrogenation reaction predominates at low temperatures, while the dehydrogenation reaction becomes more probable thermodynamically as the temperature is raised.

EXPERIMENTAL

A. Procedure. Experimental technique. 25 ml of the catalyst was placed in the catalysis tube (22 mm in diameter). The experiments were carried out in a circulating system in an electric furnace equipped with a thermoregulator. The oxygen, moisture, and other impurities were first carefully removed from the electrolytic hydrogen and the nitrogen in which the experiments were carried out.

The cyclohexene was prepared by dehydrating cyclohexanol with sulfuric acid [25]; its constants were as follows:

B.p. 82.0° (745 mm); d_4^{20} 0.811; n_D^{20} 1.4470.

Analysis. An indication of the presence of a reaction involving the redistribution of hydrogen (disproportionation) was the absence of any change in the volume of hydrogen during the reaction or of the refractive index of the catalyzate compared to that of cyclohexene. The dehydrogenation reaction was characterized by the evolution of hydrogen and an increase in the refractive index of the catalyzate over that of the initial cyclohexene. The extent of transformation of the cyclohexene was determined by analyzing the catalyzate for its percentage of cyclohexene by Kaufmann's bromometric method as perfected by Galpern

and Vinogradova [28]. Thus, knowing the per cent conversion of the cyclohexene, the change in the volume of hydrogen, and the refractive index of the catalyzate, we were able to determine quantitatively the extent to which the transformation was due to one or two of the three reactions cited above, and to compute the composition of the catalyzate.

Catalysts. In preparing the copper catalyst, we aimed at securing chemically pure copper, free of all foreign impurities, particularly nickel, and possessing a large area of contact. With this in mind, we employed double-refined electrolytic copper as the raw material for preparing our catalyst. We dissolved it in pure nitric acid and deposited it as the nitrate upon activated alumina. After the nitrate had been decomposed, we reduced to copper with hydrogen at 150-280°. The metallic copper in the catalyst totaled 15% by weight of the alumina.* Reduction to metallic iron was effected at 450° for 15 hours. The Fe weighed 15% by weight of the alumina.

B. Experimental Results. 1. Transformations of cyclohexene with a copper catalyst. Effect of temperature upon the transformations of cyclohexene in an atmosphere of hydrogen. The experiments run in the temperature range from 152 to 280°, with the cyclohexene diluted with hydrogen in the proportions of 1.3-1.5 mole of hydrogen per mole of cyclohexene, are shown graphically in Figs. 1 and 2. The conversion of cyclohexene was 22.5% at 152° (all the conversion

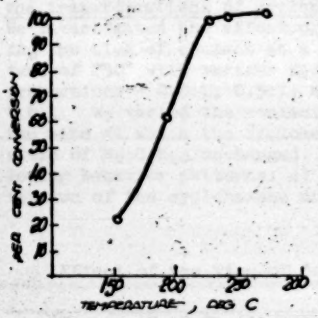

Fig. 1. Percent conversion of cyclohexene in an atmosphere of hydrogen as a function of the temperature ($Cu-Al_2O_3$ catalyst).

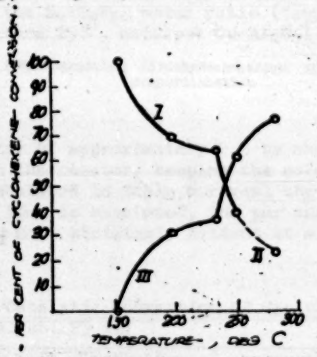

Fig. 2. Proportionate conversion of cyclohexene in an atmosphere of hydrogen as a function of the temperature ($Cu-Al_2O_3$ catalyst).

I)Hydrogenation; II)dehydrogenation; III)disproportionation

being hydrogenation), rising to 98% at 233°. As the temperature is raised, the amount of cyclohexene transformed by a redistribution (disproportionation) of the hydrogen increases, while the percentage that is hydrogenated drops off. At 280° the dehydrogenation process becomes perceptible - 23.6% of the total converted cyclohexene is dehydrogenated. Our endeavors to hydrogenate benzene under the same conditions as the cyclohexene, using a high $H_2:C_6H_6$ ratio, showed that benzene is not hydrogenated above a copper catalyst. Nor is cyclohexane dehydrogenated at 300°.

Effect of the hydrogen:cyclohexene molar ratio upon the transformation of cyclohexene. We ran a series of tests at 250° and an average cyclohexene feed rate of 3.0 ml/hr to ascertain the effect that diluting the cyclohexene with

*The iron catalyst was similarly prepared by depositing the nitrate on alumina.

hydrogen would have upon the catalytic process, the proportion of hydrogen being varied from 0.3 mole to 2.7 moles per mole of cyclohexene. Under these conditions, the cyclohexene is converted 100%. As we see from the graph, (Fig. 3), with a hydrogen dilution of 0.3:1, most of the cyclohexene is converted as the result of the hydrogen redistribution, 7% being dehydrogenated. When the molar proportion is $H_2:C_6H_{10}$ = 0.5:1, 100% of the converted cyclohexene involves the redistribution of hydrogen, while raising the proportion of hydrogen to 0.6 mole per mole of cyclohexene causes the partial hydrogenation of the cyclohexene. Any further increase in the proportion of hydrogen entails an increase in the percentage of the cyclohexene that is hydrogenated, this percentage reaching 100% at the $H_2:C_6H_{10}$ molar ratio of 2.7:1.

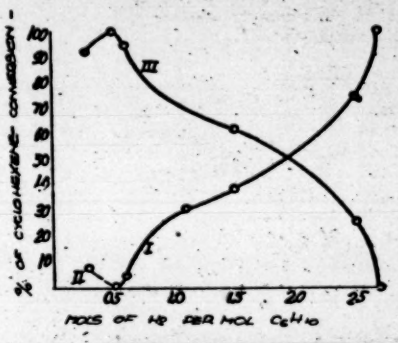

Fig. 3. Variation of the proportionate conversion of cyclohexene with the $H_2:C_6H_{10}$ molar ratio (temperature 250°, catalyst $Cu-Al_2O_3$)

I)Hydrogenation; II)dehydrogenation; III) disproportionation

Effect of the contact time upon the transformations of cyclohexene. We investigated the effect of changing the time of contact at a temperature of 250° with various $H_2:C_6H_{10}$ proportions – 0.3:1; 0.5:1; and 0.6:1. We varied the contact time by a factor of approximately 2.5 by changing the rate at which the cyclohexene was fed to the reactor, keeping the molar ratio of $H_2:C_6H_{10}$ unchanged. The figures tabulated in Table 6 reveal the following behavior patterns: a) as the contact time is shortened, the per cent conversion of the cyclohexene drops, this being most strikingly evident at a low

TABLE 6

Effect of the Time of Contact Upon the Catalytic Conversion of Cyclohexene (Volume of Catalyst: 25 ml)

Test No.	Temperature, °C	$H_2:C_6H_{10}$ molar ratio	Average C_6H_{10} feed rate, ml/hr	Contact time, seconds	Per cent conversion of C_6H_{10}	Proportion of conversion of cyclohexene, molar %		
						Hydrogenation	Disproportionation	Dehydrogenation
70	249	0.3:1	3.05	26.2	98.3	–	93.1	6.9
81	252	0.3:1	7.4	10.7	77.5	–	97.8	2.2
74	250	0.5:1	2.7	25.7	98.9	–	100.0	–
79	250	0.5:1	5.9	11.6	91.6	3.2	96.8	–
73	250	0.6:1	2.8	23.6	99.8	4.5	95.5	–
82	252	0.6:1	6.2	10.7	81.2	16.3	83.7	–

proportion of hydrogen; b) as the contact time is shortened, the proportion of the cyclohexene that is dehydrogenated drops off; and c) as the contact time is shortened, the proportion of the cyclohexene that is hydrogenated increases. Thus, a change in the contact time affects the velocity of the processes of hydrogenating and dehydrogenating the cyclohexene differently, which makes it

difficult to make a study of the kinetics of the redistribution of hydrogen in cyclohexene above copper.

Transformations of cyclohexene in an atmosphere of nitrogen. Our tests indicated that when cyclohexene, diluted with nitrogen, was passed over a Cu – Al_2O_3 catalyst, it undergoes two kinds of transformations simultaneously: a) a hydrogen redistribution, $3C_6H_{10} = 2C_6H_{12} + C_6H_6$, and b) a dehydrogenation, $C_6H_{10} = C_6H_6 + 2H_2$. In these tests in a nitrogen atmosphere we were unable to effect a 100% transformation of the cyclohexene along either of these two alternative lines, a) or b); we always observed the two reactions occurring side by side, one or the other predominating, depending upon the temperature (Fig. 4). The percentage of cyclohexene dehydrogenated rises as the temperature is raised, the percentage of cyclohexene in which the hydrogen has been redistributed dropping accordingly. It should be noted that the aggregate per cent conversion of cyclohexene in a nitrogen atmosphere is much lower than in an atmosphere of hydrogen. At 250° and with a contact time of some 12 seconds, only 24.3% of the cyclohexene is converted in nitrogen, whereas nearly 100% of the cyclohexene is converted in an atmosphere of hydrogen under the same conditions.

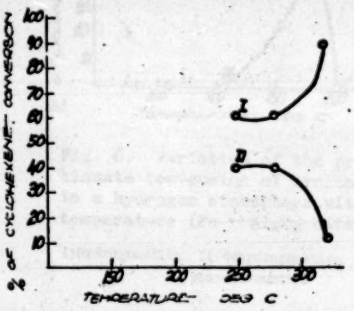

Fig. 4. Variation of the proportion of the conversion of cyclohexene in a nitrogen atmosphere with the temperature (N_2:C_6H_{10} = 1:7:1; catalyst Cu – Al_2O_3.

I) Dehydrogenation; II) disproportionation

2. Transformations of cyclohexene with an iron catalyst. The experiments on the conversion of cyclohexene with Fe – Al_2O_3 catalyst were also run in hydrogen and in nitrogen, the temperature ranging from 136 to 350° and the procedure being that employed for the copper catalyst. Our investigation of the effect of temperature (Figs. 5 and 6), of dilution with hydrogen (Fig. 7), and of the contact time indicated that the transformations of cyclohexene with iron as catalyst obey the same laws as those observed with the copper catalyst. Moreover, as with the copper catalyst, the iron catalyst is wholly unsuited to any hydrogenation of benzene or dehydrogenation of cyclohexene.

EVALUATION OF RESULTS

Our experimental results demonstrate that cyclohexene can be readily hydrogenated above copper as well as iron. When three types of transformation are present, the proportion of the cyclohexene that is hydrogenated is inversely proportional to the temperature. As the thermodynamic analysis of all three transformations indicates (Table 5), all three reactions may occur even at comparatively low temperatures (400° K), though the hydrogenation reaction has the most highly negative value of $\Delta F°$.

The reaction involved in the redistribution of the hydrogen in the cyclohexene, as a combined hydrogenation-dehydrogenation process:

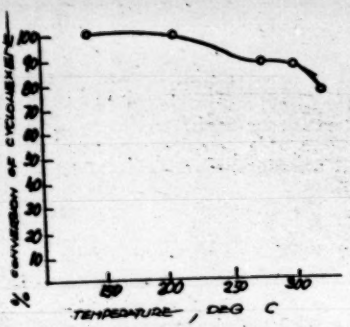

Fig. 5. Per cent conversion of cyclohexene in a hydrogen atmosphere as a function of temperature (Fe – Al_2O_3 catalyst).

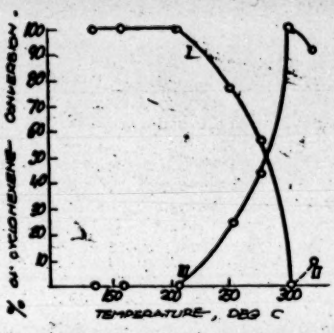

Fig. 6. Variation of the proportionate conversion of cyclohexene in a hydrogen atmosphere with the temperature (Fe – Al_2O_3 catalyst).

I)Hydrogenation; II)dehydrogenation; III) disproportionation

a) $C_6H_{10} = C_6H_6 + 2H_2$
b) $2C_6H_{10} + 2H_2 = 2C_6H_{12}$

$3C_6H_{10} = 2C_6H_{12} + C_6H_6$

takes place at a higher temperature than hydrogenation does. It should be borne in mind that the dehydrogenation of cyclohexene, which is part of the reaction involved in the redistribution of hydrogen, is rendered difficult because of the requirement that the hydrogen be detached from the $-CH_2-CH_2-$ group.

Dehydrogenation, with the evolution of gaseous hydrogen, takes place at a still higher temperature, since it is evident that the desorption of hydrogen in the gas phase requires a temperature that is even higher than that needed for the combined hydrogenation-dehydrogenation reaction.

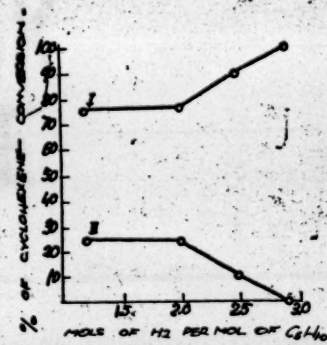

Fig. 7. Variation of the proportionate conversion of cyclohexene with the $H_2:C_6H_{10}$ molar ratio (temperature 250°; Fe – Al_2O_3 catalyst).

I)Hydrogenation; II)disproportionation

The extent of dilution with hydrogen exerts a profound effect upon the course taken by the transformation of cyclohexene. At low percentages of hydrogen, some 0.3 mole per mole of cyclohexene (experiments with a copper catalyst), dehydrogenation of the cyclohexene is observed, paralleling the predominant reaction involving the redistribution of the hydrogen. As the $H_2:C_6H_{10}$ molar ratio is increased, the proportion of cyclohexene that is hydrogenated increases, though 100% hydrogenation of the

cyclohexene is attained only with a considerable excess of hydrogen, 2.7-2.9 moles per mole of cyclohexene.

We have discovered the conditions under which all of the cyclohexene undergoes a redistribution of its hydrogen. This occurs at 250° over a copper catalyst, the dilution with hydrogen being 0.5 mol per mol of cyclohexene and the contact time being about 25 seconds; when an iron catalyst is used, this takes place only at 300° (at a high nitrogen dilution).

When these data are compared with the cited material in the literature, it becomes evident that the hydrogen in the cyclohexene is redistributed much more slowly above copper or iron than in the presence of platinum, palladium, or nickel. This is evidence of the high activity of the latter. The cyclohexane formed in the redistribution of the cyclohexene's hydrogen above copper or iron cannot be dehydrogenated in the presence of these catalysts, whereas the cyclohexane formed as the result of the redistribution of the cyclohexene's hydrogen above a platinum catalyst can be dehydrogenated to benzene at the temperatures we have employed [14]. At 200-300°, disproportionation is slow and incomplete above copper or iron.

It is essential to mention the fact that in disproportionation the per cent conversion of cyclohexene is much lower in nitrogen than in an atmosphere of hydrogen, which indicates the important role played by the presence of hydrogen at the surface of the catalyst in combined hydrogenation-dehydrogenation reactions.

The parallelism between the ease of effecting any one transformation of cyclohexene and the value of ΔF° is curious. Under any given conditions, that process will predominate for which the value of ΔF° is greatest.

The behavior of cyclohexene above the catalyst we have studied resembles its behavior above oxide catalysts (chromic oxide, vanadium oxide), above which cyclohexene is simultaneously transformed in several different ways, as has been pointed out in the cited papers by Goldwasser and Taylor [11] and Plate [13], though this transformation occurs at much higher temperatures than is the case with the copper or iron catalyst. We may, therefore, conclude that the activity of copper and iron in the catalytic transformations of cyclohexene lies between that of the metals of the platinum group and that of the oxide catalysts. The fact that copper and iron possess less activity than Pt, Pd, and Ni explains why they are unsuitable for the hydrogenation of benzene, although they are suited for use as catalysts in the hydrogenation of olefins. The chemosorption and activation of the benzene molecule are more difficult than the chemosorption of an olefin molecule, since an additional 34 Cal/mole must be expended to delocalize the bonds in the benzene molecule. This is set forth in our preceding paper [27]. Moreover, the initial stage of the hydrogenation of benzene – the addition of a molecule of hydrogen – is excluded thermodynamically (ΔF°_{470} = = +19,728 cal/mole), only the rapid hydrogen redistribution in cyclohexadiene above Pt, Pd, and Ni shifts the equilibrium [28]. Nor does the low activity of copper and iron permit the dehydrogenation of cyclohexane under the conditions enabling cyclohexene to be dehydrogenated. Here again, the splitting off of one hydrogen molecule from cyclohexane is excluded thermodynamically (ΔF°_{800} = = +10,535 cal/mole), and it is only the ensuing rapid reaction involving the disproportionation of the hydrogen in cyclohexene that shifts the equilibrium [29]. This is readily done above Pt, Pd, and Ni, but is difficult above copper or iron.

SUMMARY

1. A study has been made of the transformations of cyclohexene above copper and iron catalysts in a circulating system, with dilution by hydrogen

and nitrogen. It has been shown that copper and iron are active catalysts of the hydrogenation of cyclohexene. Under certain conditions cyclohexene is completely hydrogenated above copper at 230° and above iron at 136°.

2. It has been found that cyclohexene undergoes three kinds of transformation: a) hydrogenation to cyclohexane; b) hydrogen redistribution; and c) dehydrogenation to benzene, at the surface of a copper or iron catalyst at temperatures ranging from 130-350°, depending upon the catalysis conditions.

3. The effects of temperature, the contact time, and dilution with hydrogen or nitrogen upon the course of the cyclohexene transformations have been investigated. It has been shown that the transformation of cyclohexene in a hydrogen atmosphere may proceed wholly along one of the first two lines, depending upon the catalysis conditions, or may involve simultaneous redistribution of the hydrogen and either hydrogenation or dehydrogenation. In a nitrogen atmosphere, the transformation of cyclohexene above copper and iron catalysts involves the simultaneous redistribution of its hydrogen and dehydrogenation.

4. It has been found that the hydrogenation of benzene and the dehydrogenation of cyclohexane do not occur above copper and iron catalysts, due to their low activity. The redistribution of the hydrogen in the partially hydrogenated benzene takes place much more slowly above these catalysts than above platinum.

LITERATURE CITED

[1] A.V.Lozovoi and M.K.Dyakova, J.Gen.Chem. 10, 1 (1940).
[2] F.Truffault, Bull. Soc. chim France, [5], 1, 206-223 (1934).
[3] Sabatier, Mailhe, Ann. chim., [8] 10, 552, 555, 559 (1907).
[4] S.V.Lebedev and M.S.Platonov, J.Russ.Chem.Soc. 61, 2151 (1929); G.Vavon, Jakes, Comptes rend., 183, 299-301.
[5] A.F.Nikolaeva and P.V.Puchkov, J.Gen.Chem. 9, 2153-2155 (1939).
[6] Sigeru Tutumi, Sci. Papers Inst. Phys. Chem. Research (Tokyo). 367, 360-362 (1939).
[7] N.D.Zelinsky and G.S.Pavlov, Ber., 66, 1420 (1933).
[8] N.D.Zelinsky and Yu.A.Arbuzov, Proc. Acad. Sci. USSR, 24, 793 (1939); Yu.A.Arbuzov and N.D.Zelinsky, Proc.Acad.Sci.USSR 30, 712 (1941).
[9] N.D.Zelinsky, J.Russ.Chem.Soc., 43, 1220 (1911); N.D.Zelinsky and G.S. Pavlov, Ber., 57, 1066-1070 (1924).
[10] Böeseken, Sillevis, Proc. Koninkl. Akad. Amsterdam, 1913, 492; B.B. Corson, V.N.Ipatieff, J.Am.Chem.Soc., 61, 1056 (1939).
[11] S.Goldwesser, H.S.Taylor, J.Am.Chem.Soc., 61, 1766 (1939).
[12] A.D.Petrov, J.Russ.Chem.Soc., 60, 1435 (1928).
[13] A.F.Plate, J.Gen.Chem. 15, 156 (1945).
[14] N.A.Shcheglova and M.Ya.Kagan, J.Phys.Chem. 23, 1083 (1941).
[15] P.H.Emmet, Nis Skau, J.Am.Chem.Soc., 65, 1029 (1943).
[16] Inoue, Bull. Chem. Soc. Japan, 1, 219-226 (1926).
[17] G.B.Kistiakowsky, J.R.Ruhoff, H.A.Smith, W.E.Vaughn, J.Am.Chem.Soc. 58, 137 (1936); 58, 146 (1936).
[18] Stull, Ind.Eng.Chem. 35, 1303 (1943).
[19] K.S.Pitzer, D.W.Scott, J.Am.Chem.Soc., 65, 803 (1943).
[20] R.Spitzer, K.S.Pitzer, J.Am.Chem.Soc., 68, 2537 (1946).
[21] D.W.Scott, G.Waddington, J.C.Smith, H.M.Huffman, J.Chem.Phys., 15, 565-568 (1947).
[22] A.A.Vvedensky, Petroleum Economy, 25, No. 2, 47-50 (1947).
[23] D.R.Stull, F.D.Mayfield, Ind.Eng.Chem. 35, 639 (1943).

[24] The Physicochemical Properties of Individual Hydrocarbons, ed. Tilicheev, II, 159 (1947).
[25] Syntheses of Organic Preparations, Vol. I, 246, State Chemical Press, Moscow (1932).
[26] G.D.Galpern and E.V.Vinogradova, Chem. Solid Fuels, 8, 384 (1937).
[27] M.Ya.Kagan and S.D.Fridman, Proc. Acad. Sci. USSR, 68, 697 (1949).
[28] M.Ya.Kagan, "Problems of Kinetics and Catalysis," Trans. Conf. on Catalysis 1947, Vol. VI, p. 232, USSR Acad. Sci. Press (1949).
[29] M.Ya.Kagan and N.Shcheglova, J.Phys.Chem. 23, 1803 (1949).

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THE APPLICATION OF AMINATION BY SODIUM AMIDE TO BENZIMIDAZOLE COMPOUNDS

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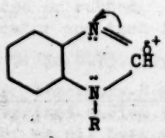
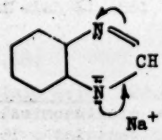
The amination of pyridine with sodium amide [1] has been extended to a fairly large number of heterocyclic systems containing the -N=CH- group [2] in the ring, as well as to some benzylidene bases [3]. There is no mention in the literature, however, of any application of this reaction to benzimidazole, its alkyl substitutes, and its derivatives. We were interested, therefore, in investigating the applicability of this reaction to the synthesis of 2-amino compounds of the benzimidazole series, on which comparatively little work has been done.

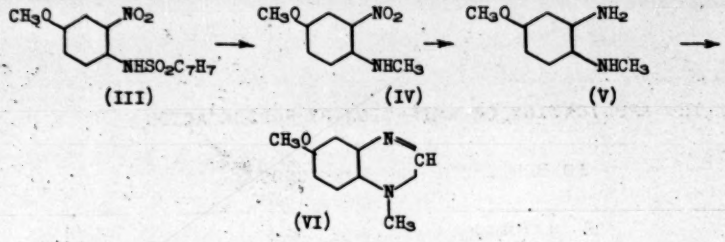
2-Aminobenzimidazole and some of its derivatives have been synthesized previously by reacting cyanogen bromide with Odphenylenediamine [4] and its respective substitution products [5]; cf [6] for its synthesis from phenylhydrazine.

We know that quinoline and some of its derivatives react with metallic amides, producing fairly high yields of the amino compounds [2]. The similarity observed in the properties of benzimidazole and quinoline compounds* would lead one to expect that it would also be fairly easy to aminate derivatives of benzimidazole. It must be borne in mind, however, that benzimidazole itself and the products of substitutions in its benzene ring contain an acid NH group in the ring, so that the action of sodium amide must first yield a sodium derivative of benzimidazole. It had to be assumed that this saltlike compound would be hard to aminate, inasmuch as the negative charge on the N atom of the imidazole ring would oppose the appearance of a partial positive charge on the carbon atom in the 2-position (cf the diagrams I and II below) and thus lessen the possibility of a reaction with a nucleophilic reagent, such as sodium amide in the present instance [8]:

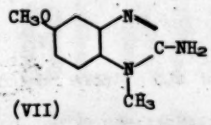
I  R = H, alkyl II 

In view of these considerations, we began a study of this reaction with derivatives of benzimidazole that were substituted at the NH group. We first synthesized 5-methoxy-1-methylbenzimidazole (VI), which has not been described in the literature before; it was easy to synthesize this compound by the method described for the 1-amino alkyl derivative of 5-methoxybenzimidazole [7], starting from the readily accessible 3-nitro-4-p-toluenesulfaminoanisole (III):

*Cf, for example, the behavior of quinaldine and 2-methylbenzimidazole in condensations with phthalic anhydride and aldehydes [8].



Our experiments have shown that amination occurs readily when 5-methoxy-1-methylbenzimidazole is heated with sodium amide in xylene. The resulting amino compound is slightly soluble in xylene and in an aqueous solution of alkali and hence may be easily recovered from the reaction mixture after the latter has been processed with a solution of soda. The yield is 60%. The compound forms azomethin with o-nitrobenzaldehyde, proving that it contains a primary amino group. No diazonium salts are formed when a solution of the amine in hydrochloric acid is treated with nitric acid; hence, the amino group is located in the imidazole ring, as we had assumed. Thus, the amination product had to have either the structure of 2-amino-5-methoxy-1-methylbenzimidazole (VII) or the tautomeric 5-methoxy-1-methylbenzimidazolonimide:



These results indicate that amination with sodium amide may be employed to introduce an amino group at the 2-position in 1-alkyl-substituted benzimidazoles.

EXPERIMENTAL

Sodium salt of 3-nitro-4-p-toluenesulfaminoanisole. 28.8 g of 3-nitro-4-p-toluenesulfaminoanisole was dissolved in 100 ml of alcohol and 10 g of 46% sodium hydroxide dissolved in 65 ml of alcohol was gradually added to the hot (70°) solution. Lustrous, bright-red crystals settled out of the dark-red solution when it was seeded or rubbed. They were filtered out, washed with alcohol, and dried in a desiccator and then in a drying cabinet at 100°.

Found %: Na 6.73. $C_{14}H_{13}N_2O_5SNa$. Computed %: Na 6.68.

2-Nitro-4-methoxy-N-methylanilide of p-toluenesulfonic acid. 22.4 g of the finely pulverized sodium salt of 3-nitro-4-p-toluenesulfaminoanisole was heated to 130° over an oil bath with 13 g of the methyl ester of p-toluenesulfonic acid and kept at that temperature for half an hour. Then 65 ml of alcohol was added, and the mixture was boiled for 2 hours. The alcohol was driven off, and the residue was stirred with hot water, filtered out, and washed with water. Yield 21.6 g. Yellowish-white, lustrous crystals with a m.p. of 122-123° (from alcohol), readily soluble in acetone and benzene.

Found %: S 9.45, 9.43. $C_{15}H_{16}N_2O_5S$. Computed %: S 9.53.

3-Nitro-4-methylaminoanisole (IV). 3 g of the 2-nitro-4-methoxy-n-methylanilide of p-toluenesulfonic acid was gradually added to 10 ml of sulfuric acid (sp. gr. 1.84). The next day the solution was heated for 30 minutes to 60° and

poured into 100 ml of water while still warm. Red crystals precipitated out. The mixture was alkalinized with a concentrated solution of ammonia, and the precipitate was filtered out and washed with water. The yield exceeded 95%. Bright-red crystals (from alcohol), with a m.p. of 97-98°, readily soluble in benzene and acetone, slightly soluble when heated in water.

Found %: N 15.59, 15.62. $C_8H_{10}N_2O_3$. Computed %: N 15.38.

3-Amino-4-methylaminoanisole (V). 3.0 g of 3-nitro-4-methylaminoanisole and 5 g of tin were placed in a flask, and 20 ml of concentrated hydrochloric acid, diluted with an equal volume of water, was gradually added with stirring. After reduction was complete, the reaction mixture was heated over a water bath until nearly all the tin had dissolved. After it had cooled, it was treated with an excess of 40% sodium hydroxide and extracted with ether. Driving off the ether left the diamine behind as a dark crystalline mass. Yield: 2.4 g. The diamine may be secured in a purer state by concentrating the ether solution to small volume, filtering out the precipitate that settles out upon cooling, and washing it with ether.* Double recrystallization from gasoline yielded the compound as nearly colorless needles with a m.p. of 78.3-78.8°, readily soluble in benzene and alcohol, which turned pink when exposed to the air. Adding sodium nitrite to a solution of the diamine in hydrochloric acid turns the solution an intense crimson.

Found %: C 63.22, 63.01; H 8.00, 7.94. $C_8H_{12}N_2O$. Computed %: C 63.13; H 7.95.

5-Methoxy-1-methylbenzimidazole (VI). 9 g of 3-nitro-4-methylaminoanisole was reduced with tin and hydrochloric acid as described above; the reaction mixture was then alkalinized and extracted with benzene. The benzene extract was shaken up with 10% hydrochloric acid; alkalinizing the hydrochloric-acid solution yielded the diamine as an oil that crystallized when rubbed. The crystals were filtered out, washed with water, and immediately mixed with 15 ml of 80% formic acid, the mixture being heated to the boil for 1.5 hours over an oil bath. The resultant solution was diluted with water, boiled with charcoal, filtered, and alkalinized with sodium hydroxide. The 5-methoxy-1-methylbenzimidazole was recovered as brownish-pink crystals. Yield 7.4 g (80%). White crystals (from benzene) with a m.p. of 112-113°, soluble in water, alcohol, acetone, and ether.

Found %: N 17.20. $C_8H_{10}ON_2$. Computed %: N 17.27.

The picrate consisted of yellow needles (from glacial acetic acid) with a m.p. of 256-257°.

2-Amino-5-methoxy-1-methylbenzimidazole (VII). 3 g of 5-methoxy-1-methylbenzimidazole and 1.6 g (based on 100%) sodium amide were heated to boiling for 2 hours in 25 ml of anhydrous xylene. Soon after heating began large amounts of hydrogen were evolved. When the mixture cooled, 30 ml of a 10% soda solution was added. The 2-amino derivative, which was slightly soluble in the cold in xylene and in the alkaline solution, was in the precipitate. It was filtered out, and washed with xylene, a soda solution, and a small quantity of water. The resultant brownish-gray substance (2.25 g) was dissolved in alcohol, the solution being filtered while hot. Then the alcohol was driven off, and the residue was dissolved in 5% hydrochloric acid. Activated charcoal was added, and the solution was heated to boiling and then filtered. Alkalinizing the solution with a solution of soda yielded pale-pink crystals. Yield 1.95 g (60%). The substance was purified by crystallization from alcohol and a large volume of benzene. Colorless, lustrous needles (from benzene) with a m.p. of 222-222.5°

*Also see the description of the synthesis of 5-methoxy-1-methylbenzimidazole for the recovery of diamine.

(with decomposition), slightly soluble in ether or cold water, and very slightly soluble in a 10% aqueous solution of sodium hydroxide. When it was reacted in alcohol with picryl chloride and sodium acetate, a precipitate of the yellow picryl derivative was rapidly thrown down.

Found %: N 23.82, 23.76. $C_9H_{11}ON_3$. Computed %: N 23.72.

The picrate consisted of minute yellow needles (from glacial acetic acid) with a decomposition temperature of 299°.

2-(2'-Nitrobenzylidene)-amino-5-methoxy-1-methylbenzimidazole. This compound was synthesized by heating 2-amino-5-methoxy-1-methylbenzimidazole in alcohol with an equivalent quantity of 2-nitrobenzaldehyde; it was purified by crystallization from alcohol. Orange-red needles with a m.p. of 172-172.5°.

Found %: N 18.13. $C_{16}H_{14}O_3N_4$. Computed %: N 18.06.

SUMMARY

It has been shown that the amination of heterocyclic compounds with sodium amide may be extended to the 1-alkyl substitutes of benzimidazole.

LITERATURE CITED

[1] A.E.Chichibabin and O.A.Zeide, J.Russ.Phys.Chem.Soc., 46, 1216 (1914).

[2] Organic Reactions, Vol. I, p. 115. State Press for Foreign Literature. (1948).

[3] A.V.Kirsanov and Ya. N. Ivashchenko, J.Gen.Chem. 5, 1494 (1935).

[4] P. Pierron, Ann. chim. phys., (8), 15, 189, 193 (1908).

[5] German Patent 641,598, Chem. Zentr., (1937) 1, 3716; N. Leonard, Curtin, Beck, J.Am.Chem.Soc., 69, 2459 (1947).

[6] G.Pellizzari, A. Gaiter, Gazz., 48, II, 151 (1918).

[7] A.M.Simonov, J.Gen.Chem. 10, 1588 (1940).

[8] E.Bamberger, B.Berle, Ann., 273, 303 (1893).

[9] Cf: F. Bergstrom, J.Org. Chem. 3, 233 (1938); C. Deasy, J.Org.Chem., 10, 141 (1945).

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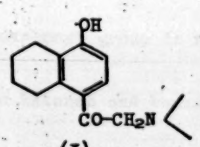
AMINO KETONES OF THE TETRAHYDRONAPHTHALENE SERIES

SYNTHESIS OF ar-1-HYDROXY-4-(AMINOACETO)-TETRAHYDRONAPHTHALENES

S. I. Sergievskaya and R. G. Vdovina

The amino ketones with the structure $\underline{Ar}CO(CH_2)_n$ N< are the initial substances for the synthesis of some of the most important pharmaceuticals. Not much work has been done on this type of compound in the tetrahydronaphthalene series; we set as our goal the synthesis of ar-1-hydroxy-4-(aminoaceto)-tetrahydronaphthalenes (I) containing amino groups of various structures.

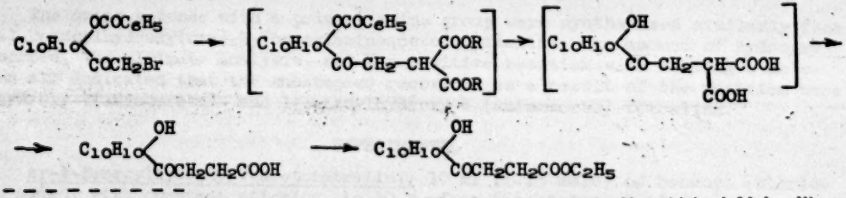
The commonest method of synthesizing amino ketones of this sort is condensing the respective halogen ketones with amines.



(I)

We used ar-1-hydroxy-4-acetotetralin, which we had available, to produce the halogen ketone we required. Inasmuch as two atoms of bromine are simultaneously added to the molecule when a similar naphthalene compound – 1-hydroxy-4-acetonaphthalene – is brominated, one entering the ring and the other the side chain [1], whereas only the side chain is brominated in the bromination of 1-benzoylhydroxy-4-acetonaphthalene [2], we used 1-benzoyl-hydroxy-4-acetotetralin in the reaction to avoid the bromination of the ring, and secured a monobromo compound that proved to be 1-benzoyl-hydroxy-4-(bromaceto)-tetralin.*

We determined the position of the bromine by condensing this compound with sodium malonic ester, followed by other transformations as outlined below in the diagram; this yielded 1-hydroxy-4-tetrahydronaphthoylpropionic acid and its ethyl ester, which were identical with the compounds previously synthesized by a different method [3].



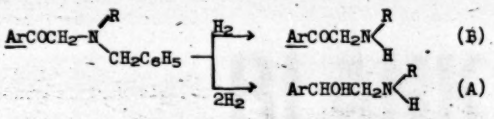
*We ran supplementary experiments on the bromination of 1-hydroxy-4-acetotetralin, which yielded a dibromo compound, as in the naphthalene series, the structure of which we did not determine.

Reacting 1-benzoylhydroxy-4-(bromaceto)-tetralin with diethylamine, methylamine, benzylamine, and benzylmethylamine yielded the respective aminoketones without any special difficulty. The benzoyl group was then saponified with alcoholic solutions of hydrogen chloride. Saponification with hydrohalic acids of various concentrations produced much lower yields.

All the amino ketones described in this paper were isolated as their hydrochlorides, some of them also as picrates; efforts to secure the amino ketones in the chemically individual state from the hydrochlorides of the bases met with failure.

The ready condensation of aryl halogen alkyl ketones with benzylamines and with alkylbenzylamines is often utilized in the synthesis of aliphatic-aromatic aminoketones or of aryl amino alcohols with secondary or primary amino groups, since the benzyl group is readily split off as toluene during the catalytic hydrogenation of benzyl alkyl amino ketones (or benzyl amino ketones).

The course of this hydrogenation may vary, depending upon the structure of the original substance, the nature and activity of the catalyst, and the other reaction conditions. Very often, splitting off the benzyl group is paralelled by the reduction of the carbonyl group, and amino alcohol (A) being formed, but in many instances the reaction proceeds in stages, the benzyl group being split off first and an alkyl amino ketone or an amino ketone (B) being formed.



It is stated in the literature [4] that sometimes the carbonyl group is reduced first, the benzyl group being split off afterwards.

We hydrogenated benzoylhydroxy(oxy)-benzyl methyl amino ketones and benzoylhydroxy(oxy)-benzyl amino ketones.

The catalyst used was 8-10% palladium on charcoal; the reaction was carried out at atmospheric pressure and a temperature of 27-30°, and methanol or ethyl alcohol was used as a solvent. It was easier to hydrogenate unbenzoylated amino ketones. Hydrogenation of 1-benzoylhydroxy-4-(benzylmethylaminoaceto)-tetralin with ensuing saponification of the benzoyl group, as well as hydrogenation of the respective amino ketone with a free hydroxy group, yielded ar-1-hydroxy-4-(methylaminoaceto)-tetralin, which was identical with the amino ketone synthesized by condensing 1-benzoylhydroxy-4-(bromaceto)-tetralin with methylamine and then saponifying the benzoyl group. The identity of the resultant substances was definite proof that the catalytic hydrogenation of these amino ketones, which contain a benzyl group, takes place in stages under the foregoing conditions, with the benzyl group being split off first of all.

The amino ketones with a primary amino group were synthesized similarly from ar-1-benzoylhydroxy(oxy)-4-(benzylaminoaceto)-tetralins; the amount of hydrogen absorbed, the ultimate analysis, and the positive reaction with Fehling's solution all indicated that the substances recovered as a result of the reaction were 1-hydroxy-4(aminoaceto)- and 1-benzoylhydroxy-4-(aminoaceto)-tetralins.

EXPERIMENTAL

ar-1-Benzoylhydroxy-4-acetotetralin. 10 ml (1.13 mole) of benzoyl chloride was added, with constant stirring, to 10 g of ar-1-acetotetralol* dissolved in 50 ml of desiccated pyridine, chilled externally by ice. The reaction mixture

*Prepared in accordance with the description furnished by S. I. Sergieva and L. M. Morozovskaya [5].

was allowed to stand for 6 hours at room temperature, after which it was poured over an ice-water mixture, and hydrochloric acid was added. The mixture was extracted several times with ether, and the ether solution was washed with 10% hydrochloric acid and with water and desiccated with sodium sulfate. The ether was then driven off, and the residue – 14 g of a faintly colored powder with a m.p. of 111-113° – was recrystallized from alcohol. This yielded 10.5 g (61% of the theoretical) of a substance with a m.p. of 115-116°. Colorless crystals, soluble in acetone, benzene, toluene, chloroform, and ether at room temperature and in hot ethyl alcohol and methanol.

3.417 mg substance: 9.712 mg CO_2; 1.894 mg H_2O. Found %: C 77.52; H 6.20. $C_{18}H_{18}O_3$. Computed %: C 77.55; H 6.12.

ar-1-Benzoylhydroxy-4-bromacetotetralin. 1.8 ml (2 moles) of bromine was added to 10 g of ar-1-benzoylhydroxy-4-acetotetralin dissolved in 50 ml of chloroform. The mixture was heated briefly over a warm water bath (25-30°), hydrogen bromide being evolved.

The chloroform was driven off in vacuum to dryness, after which air was blown through the flask until all the hydrogen bromide had been eliminated, and the residue was recrystallized from carbon tetrachloride. This yielded 7.75 g (62.5% of the theoretical) of a substance with a m.p. of 128-129° (with decomposition). Lustrous colorless crystals, readily soluble in acetone, chloroform, and ethyl acetate, more sparingly soluble in ethyl alcohol or methanol, and insoluble in ether or petroleum ether.

4.910 mg substance: 2.445 mg AgBr. 6.175 mg substance: 3.110 mg AgBr (Carius). Found %: Br 21.19, 21.43. $C_{18}H_{17}O_3Br$. Computed %: Br 21.43.

Proof of the structure of the synthesized ar-1-benzoylhydroxy-4-bromacetotetralin. 0.3 g of finely powdered sodium and 3 ml of benzene were placed in a three-necked flask, fitted with a reflux condenser and a stirrer. The flask was heated, with stirring for 10-15 minutes over a water bath, after which 2.1 g of malonic ester was gradually added. Heating was continued for some time, after which 3 g of 1-benzoylhydroxy-4-bromacetotetralin dissolved in 25 ml of benzene was added to the resulting suspension. The reaction mass was heated for 4 hours with constant stirring, water was added, and the benzene solution was decanted, washed again with water, and desiccated with sodium sulfate, after which the ether and the benzene were driven off. The residue of 5.4 g – a light yellow powdery mass – was saponified, without further purification, by heating it with 8.5 ml of a 10% water-methanol solution of potassium hydroxide.

After the alcohol had been driven off in vacuum, the residue which smelled like methyl benzoate, was diluted with water and extracted with ether. The aqueous-alkaline solution was filtered and acidulated. A flocculent precipitate and a dark-red oil were precipitated, the oil solidifying when rubbed. Recrystallization from a benzene-alcohol mixture yielded a substance with a m.p. of 157-159°, the composition of which approximated that of hydroxytetralylacetomalonic acid.

0.9 g of the presumed hydroxytetralylacetomalonic acid was dissolved in 12 ml of pyridine and heated over an oil bath (120-125°) until no more carbon dioxide was evolved. The pyridine was driven off, and the residue (a dark oil) was washed with 10% hydrochloric acid. A dark precipitate was thrown down, which was dissolved by heating it with a 10% solution of soda; the solution was filtered, and the filtrate was acidified with 10% hydrochloric acid. The resultant precipitate (0.4 g) fused at 182-187°.

Recrystallization, first from water, and then from a benzene-alcohol mixture, yielded 0.2 g of a substance with a m.p. of 190-191°; a test sample of this

ubstance, mixed with 1-hydroxytetrahydronaphthoyl-4-propionic acid produced by a different method, exhibited no depression.

0.1 g of the substance with a m.p. of 190-191°, synthesized as set forth above, was dissolved in 2 ml of absolute ethyl alcohol, one drop of concentrated sulfuric acid was added, and the whole was heated for several hours over a water bath; the alcohol was then driven off in vacuum, the residue was dissolved in ether, and the ether solution was washed with a 3% solution of bicarbonate and with water and desiccated with Na_2SO_4. The ether was then driven off, and the residue recrystallized from methanol. A colorless powder with a m.p. of 121-123°. A test sample of this substance, mixed with the ethyl ester of 1-hydroxy-4-tetrahydronaphthoylpropionic acid, exhibited no depression.

4.321 mg substance: 10.975 mg CO_2; 2.728 mg H_2O. Found %: C 69.27; H 7.07. $C_{18}H_{20}O_4$. Computed %: C 69.56; H 7.24.

ar-1-Benzoylhydroxy-4-(benzylmethylaminoaceto)-tetrahydronaphthalene hydrochloride. 9 g of ar-1-benzoylhydroxy-4-bromacetotetralin and 27 ml of benzene were placed in a three-necked flask fitted with a reflux condenser and a stirrer. The reaction mixture was stirred, and 6 g (2 moles) of benzylmethylamine was gradually added to the mixture. As the benzylmethylamine was added, the mixture warmed up somewhat, and a crystalline precipitate was thrown down – benzylmethylamine hydrobromide. Stirring was continued for 3 hours at room temperature, and then the reaction mixture was allowed to stand for 12-15 hours, after which the benzylmethylamine hydrobromide was filtered out, washed with small batches of benzene, and desiccated. This yielded 4.4 g (95% of the theoretical) with a m.p. of 165-166°.

The benzene was driven out of the benzene filtrate in vacuum; the residue was a thick red mass totaling 9.4 g. Absolute ether was added to this residue, but the latter did not dissolve completely.* The brightly colored ether solution was filtered, and an ether solution of hydrogen chloride was cautiously added, with constant stirring and efficient chilling, until no more of the curdled yellow precipitate was thrown down; the latter was filtered out, washed with absolute ether, and dried in a vacuum desiccator. This yielded 6.3 g of a substance with m.p. 183-186°.

After recrystallization from an acetone-methanol mixture, the ar-1-benzoyl-4-(benzylmethylaminoaceto)-tetralin was a colorless crystalline precipitate with a m.p. of 192-194° (with decomposition). In determining the melting point, the apparatus was preheated to 170°. The yield was 3.4 g (32% of the theoretical).

The substance is fairly readily soluble in methanol, but more sparingly in ethyl alcohol; it is insoluble in acetone, benzene, or ether. Its aqueous solution is readily hydrolyzed.

4.079 mg substance: 10.769 mg CO_2; 2.277 mg H_2O. 3.711 mg substance: 9.760 mg CO_2; 1.950 mg H_2O. 9.052 mg substance: 0.245 ml N_2 (20.5°, 751 mm). 8.145 mg substance: 0.230 ml N_2 (20.5°, 751 mm). 8.800 mg substance: 2.795 mg AgCl. Found %: C 71.69, 71.72; H 6.22, 5.88; N 3.11, 3.25; Cl 7.85. $C_{27}H_{27}O_3N \cdot HCl$. Computed %: C 72.1; H 6.23; N 3.11; Cl 7.89.

The picrate. 2 g of ar-1-benzoylhydroxy-4-(benzylmethylaminoaceto)-tetralin hydrochloride was heated in 20 ml of methanol, and 45 ml of an alcoholic solution of sodium bicarbonate was added to the solution. The whole was allowed to stand for 2 hours, after which the solvent was driven off, the residue (a red oil) was dissolved in ether, and the resulting solution was filtered, washed with water, and desiccated with Na_2SO_4. The ether was then driven off. The residue was the base ar-1-benzoylhydroxy-4-(benzylmethylaminoaceto)-tetralin as a red oil. 1 g of the unpurified base was dissolved by heating it in 5 ml of absolute ethyl

*If the residue is allowed to stand for a long time, it crystallizes into a hyaline mass that is hard to process.

alcohol, and 1.5 g of picric acid (2.7 moles) dissolved in 40 ml of alcohol was added. The solution was set aside to stand overnight. A red oil formed on the bottom of the flask; the alcoholic solution was separated from the oil and again allowed to stand for 3-4 days. A yellow precipitate settled; it was filtered; m.p. 131-135°. Its m.p. was 137-138° after recrystallization from alcohol. Yield 0.3 g. A yellow powder, soluble in acetone, alcohol, ethyl acetate, and (by heating) in water.

6.905 mg substance: 4.34 ml 0.01 N H_2SO_4. 7.638 mg substance: 4.70 ml 0.01 N H_2SO_4 (Kjeldahl). Found %: N 8.80, 8.61. $C_{33}H_{30}O_{10}N_4$. Computed %: N 8.73.

ar-1-Hydroxy-4-(benzylmethylaminoaceto)-tetralin hydrochloride. 3 g of ar-1-benzoylhydroxy-4-(benzylmethylaminoaceto)-tetralin hydrochloride was placed in a round-bottomed flask fitted with a reflux condenser and dissolved in 6 ml of methanol, after which 9 ml of a 30% methanol solution of hydrogen chloride was added. The mixture was heated over a water bath for 10-16 hours. The alcohol was driven off in vacuum to dryness. A 10% ammonia solution was added to the residue (a red hyaline mass), and the whole was extracted with ether (while warmed slightly) until all the residue had dissolved in the ether. The ether layer was washed with water and desiccated with sodium sulfate. The drying agent was filtered out, and a dilute ether solution of hydrogen chloride was added to the filtrate, with efficient stirring and chilling. A curdled yellow precipitate was thrown down; it was filtered out, washed with ether, and quickly transferred to acetone, since the precipitate disintegrated in the air; the acetone was heated and vigorously stirred with a rod, which turned the crumbling mass into a powder. The latter was filtered out and washed with acetone. This yielded 1.1 g (50% of the theoretical) of a nearly colorless substance with a m.p. of 198.0-201° (with decomposition). Recrystallization from alcohol yielded the ar-1-hydroxy-4-(benzylmethylaminoaceto)-tetralin hydrochloride as lustrous colorless crystals with a m.p. of 199-201.5° (with decomposition). Its aqueous solutions are readily hydrolyzed.

10.949 mg substance: 3.12 ml 0.01 N H_2SO_4. 10.807 mg substance: 4.19 ml 0.01 N H_2SO_4, (Kjeldahl). 7.300 mg substance: 3.14 mg AgCl. 5.790 mg substance: 2.390 mg AgCl. Found %: Cl 10.64, 10.21; N 3.99, 4.19. $C_{20}H_{23}O_2N \cdot HCl$. Computed %: N 4.03; Cl 10.3.

ar-1-Benzoylhydroxy-4-(methylaminoaceto)-tetralin hydrochloride. 0.8 g of ar-1-benzoylhydroxy-4-(benzylmethylaminoaceto)-tetralin hydrochloride, dissolved by heating it in 20 ml of methanol, and 1.2 g of a catalyst (10% palladium on charcoal)* were placed in a reducing bottle. After the bottle had been filled with hydrogen, the mixture was agitated. The catalyst was filtered out and washed with methanol. The methanol was driven off in vacuum to dryness. The 0.35 g of residue (50% of the theoretical) was recrystallized from alcohol, yielding ar-1-benzoylhydroxy-4-(methylaminoaceto)-tetralin hydrochloride with a m.p. of 223-225° (with decomposition). The hydrochloride consisted of colorless lustrous crystals, soluble in methanol, less so in ethyl alcohol. Its aqueous solution is readily hydrolyzed.

7.254 mg substance; 0.248 ml N_2 (22.5°, 739.5 mm). 2.510 mg substance: 1.000 mg AgCl. 7.135 mg substance: 2.805 mg AgCl. Found %: Cl 9.85, 9.8; N 3.84. $C_{20}H_{21}O_3N \cdot HCl$. Computed %: N 3.89; Cl 9.88.

*10% palladium on charcoal was prepared as follows: 5 g of activated animal charcoal in 30-35 ml of water and 1 g of palladium chloride, dissolved in 6-7 ml of water, were placed in a bottle used for reducing, and a few drops of hydrochloric acid were added. The mixture was agitated in a current of hydrogen for 1 hour. 300 ml of hydrogen were absorbed. The catalyst was filtered out, washed with warm water, and dried in a vacuum dessicator.

ar-1-Hydroxy-4-(methylaminoaceto)-tetralin hydrochloride. a) 1.8 g of ar-1-hydroxy-4-(benzylmethylaminoaceto)-tetralin hydrochloride, dissolved by heating it in 25 ml of methanol, and 2.7 g of the catalyst (10% palladium on charcoal) were placed in a bottle used for reducing. The bottle was filled with hydrogen, and the mixture agitated in a current of hydrogen. When no more hydrogen was absorbed, the catalyst was filtered out and washed with methanol. The alcohol was then driven off in vacuum to dryness. The residue – a white deposit totaling 1 g (70% of the theoretical) – was recrystallized from alcohol. Recrystallization yielded 0.65 g (50% of the theoretical) of a substance with a m.p. of 232-233.5° (with decomposition). ar-1-Hydroxy-4-(methylaminoaceto)-tetralin hydrochloride consisted of colorless lustrous crystals that are soluble in methanol and ethyl alcohol, and in water (when heated).

5.290 mg substance: 2.915 mg AgCl. 7.100 mg substance: 0.348 ml N_2 (24°, 733 mm). Found %: C 13.63; N 5.44. $C_{13}H_{17}O_2N \cdot HCl$. Computed %: Cl 13.88; N 5.48.

b) 1 g of ar-1-benzoylhydroxy-4-(methylaminoaceto)-tetralin hydrochloride, dissolved in 10 ml of methanol, was placed in a round-bottomed flask fitted with a reflux condenser, and 5 ml of a 30% methanol solution of hydrogen chloride was added. The mixture was heated over a water bath for 10-12 hours. The alcohol was then driven off in vacuum to dryness. The gray residue was recrystallized from alcohol. This yielded 0.2 g (26.6% of the theoretical) of ar-1-hydroxy-4-(methylaminoaceto)-tetralin hydrochloride, with a m.p. of 230-232.5°.

Its solubility was the same as described in Experiment (a).

7.034 mg substance: 0.354 ml N_2 (23°, 736 mm). Found %: N 5.62. $C_{13}H_{17}O_2N \cdot HCl$. Computed %: N 5.48.

Synthesis of ar-1-benzoylhydroxy-4-(methylaminoaceto)-tetralin hydrochloride by condensing ar-1-benzoylhydroxy-4-bromacetotetralin with methylamine. 3 g of ar-1-benzoylhydroxy-4-bromacetotetralin (m.p. 128-129°) and 20 ml of absolute benzene were placed in a three-necked flask, fitted with a reflux condenser, a stirrer, and a dropping funnel. The mixture was stirred and chilled and 0.5 g of methylamine (2 moles) in 5 ml of absolute benzene was added. Methylamine hydrobromide was seen to form within a short interval, the color of the reaction mass undergoing a change. The reaction mixture was then stirred for 3 hours, the methyl hydrobromide was filtered out and washed with benzene, and the solvent was driven off in vacuum. The residue – a red mass – was dissolved in absolute ether. The ether solution was filtered and well chilled, and an ether solution of hydrogen chloride was added to it, with vigorous stirring, until its reaction to Congo red was acid. The resulting precipitate adhered to the wall of the beaker, so that the ether solution was decanted, and the substance remaining was triturated with acetone. This yielded a white friable powder, which was filtered out and washed with acetone and with ether, yielding 0.4 g (14% of the theoretical) of a substance with a m.p. of 223-225°. The resultant ar-1-benzoylhydroxy-4-(methylaminoaceto)-tetralin hydrochloride was soluble in methanol, very slightly soluble in ethyl alcohol, and insoluble in acetone. Its aqueous solution hydrolyzed readily. These are the properties of the substance prepared by reducing the hydrochloride of ar-1-benzoylhydroxy-4-(benzylmethylaminoaceto)-tetralin.

Saponification of the benzoyl group. 0.5 g of the ar-1-benzoylhydroxy-4-(methylaminoaceto)-tetralin hydrochloride was placed in a round-bottomed flask fitted with a reflux condenser, and 50 ml of a 20% solution of hydrogen chloride in ethyl alcohol was added. The mixture was heated over a boiling water bath for 12 hours, after which the alcohol was driven off in vacuum. The residue, an oily red substance, was triturated with acetone. The resulting white powder was filtered out and washed, first with acetone and then with ether. This yielded

0.25 g (70% of the theoretical) of a substance with a m.p. of 234-236°. The solubility of the ar-1-hydroxy-4-(methylaminoaceto)-tetralin hydrochloride was the same as that of the preparation synthesized by reducing the hydrochloride of ar-1-hydroxy-4-(benzylmethylaminoaceto)-tetralin.

4.792 mg substance: 0.235 ml N_2 (25°, 739.4 mm). 6.478 mg substance: 3.615 mg AgCl. Found %: N 5.46; Cl 13.81. $C_{13}H_{17}O_2N \cdot HCl$. Computed %: Cl 13.88; N 5.48.

ar-1-Benzoylhydroxy-4-(benzylaminoaceto)-tetralin hydrochloride. 5 g of ar-1-benzoylhydroxy-4-bromoacetotetralin (m.p. 128-129°) and 25 ml of absolute benzene were placed in a three-necked flask, fitted with a reflux condenser and a stirrer. The mixture was stirred while the flask was chilled with ice. 2.9 g of benzylamine (2 moles) were added to the stirred and chilled suspension, after which the reaction mixture was stirred for 3.5 hours. The benzylamine hydrobromide was rapidly filtered out and washed with benzene; this yielded 2.2 g (85% of the theoretical) with a m.p. of 208-210°. The benzene solutions were distilled in a 10-12 mm vacuum over a water bath. The residue left after the benzene had been driven off was at once treated, while still hot, with absolute ether. The benzylamine hydrobromide precipitate (0.1 g) was filtered out of the ether solution, and an ether solution of hydrogen chloride was added to the filtrate, with vigorous stirring and chilling, until the latter's reaction with Congo red was acid. The resulting yellow precipitate was filtered out, washed with absolute ether, and pressed out. This yielded 4.5 g (78% of the theoretical). The precipitate crumbled somewhat when exposed to the air, but it became entirely friable after drying in a vacuum desiccator. The synthesized substance was then heated with a minimum quantity of acetone; after the mixture had cooled, the undissolved substance was filtered out. M.p. 183-186°. Yield 2.9 g (50% of the theoretical). Recrystallization from absolute alcohol yielded 2 g (34.5% of the theoretical) or ar-1-benzoylhydroxy-4-(benzylaminoaceto)-tetralin hydrochloride, a colorless crystalline substance with a m.p. of 194.5-196° (with decomposition, in an apparatus preheated to 180°).

The hydrochloride of ar-1-benzoylhydroxy-4-(benzylaminoaceto)-tetralin is soluble in methanol, more sparingly so in ethyl alcohol, and insoluble in acetone, benzene, or ether. Its aqueous solution is readily hydrolyzed.

6.781 mg substance: 0.206 ml N_2 (22.5°, 726 mm). 6.007 mg substance: 0.185 ml N_2 (21°, 731.1 mm). 4.364 mg substance: 1.482 mg AgCl. Found %: N 3.35, 3.44; Cl 8.4. $C_{26}H_{25}O_3N \cdot HCl$. Computed %: N 3.22; Cl 8.15.

ar-1-Hydroxy-4-(benzylaminoaceto)-tetralin hydrochloride. 3 g of ar-1-benzoylhydroxy-4-(benzylaminoaceto)-tetralin hydrochloride. was placed in a round-bottomed flask fitted with a reflux condenser and dissolved in 6 ml of methanol, and 9 ml of a 30% solution of hydrogen chloride in methanol was added. The whole was heated over a water bath for 12-15 hours. The alcohol was then driven off in vacuum to dryness. The residue, 1.6 g (77% of the theoretical) of a gray crystalline substance, was recrystallized from absolute alcohol. This yielded 1 g (43% of the theoretical) of ar-1-hydroxy-4-(benzylaminoaceto)-tetralin hydrochloride, with a m.p. of 201.5-203° (with decomposition, in an apparatus preheated to 180-190°). ar-1-Hydroxy-4-(benzylaminoaceto)-tetralin hydrochloride consists of colorless, lustrous crustals, soluble in methanol, less so in ethyl alcohol. Its aqueous solution is readily hydrolyzed.

5.087 mg substance: 0.191 ml N_2 (21°, 735 mm). 4.988 mg substance: 0.185 ml N_2 (21°, 735 mm).
6.743 mg substance. 2.870 mg AgCl. Found %: N 4.21, 4.16; Cl 10.53. $C_{18}H_{21}O_2N \cdot HCl$. Computed %: N 4.22; Cl 10.71.

ar-1-Benzoylhydroxy-4-(aminoaceto)-tetralin hydrochloride. 1 g of ar-1-benzoylhydroxy-4-(benzylaminoaceto)-tetralin hydrochloride, dissolved in 15 ml of absolute methanol, and 2 g of a catalyst (10% palladium on charcoal) were placed in a reducing bottle. After the bottle had been filled with hydrogen, the mixture was shaken up at 25-27°. 30 ml of hydrogen was absorbed in 4 hours (the theoretical quantity). The catalyst was filtered out and washed with methanol. The alcohol was then driven off in vacuum to dryness, the residue being recrystallized from an acetone-methanol mixture. ar-1-Benzoylhydroxy-4-(aminoaceto)-tetralin hydrochloride consists of colorless, lustrous crystals, with a m.p. of 202.5-204°, soluble in methanol and ethyl alcohol. Its aqueous solution is readily hydrolyzed.

5.180 mg substance: 0.168 ml N_2 (20°, 740.5 mm). 6.516 mg substance: 0.209 ml N_2 (19.5°, 744 mm). Found %: N 3.69, 3.67. $C_{18}H_{18}O_3N \cdot HCl$. Computed %: N 4.04

ar-1-Hydroxy-4-(aminoaceto)-tetralin hydrochloride. 1 g of ar-1-hydroxy-4-(benzylaminoaceto)-tetralin hydrochloride, dissolved in 25 ml of 96° alcohol, and about 5 g of Pd on charcoal were placed in a bottle used for reducing. Hydrogenation was carried out at 25-27°. After the absorption of hydrogen had ceased, the catalyst was filtered out and washed with alcohol, and the solvent was driven off in vacuum. The residue, an oily substance, was triturated with absolute ether, yielding 0.3 g (42% of the theoretical) of a fraible gray powder. This powder was dissolved in absolute alcohol and precipitated with absolute ether; this procedure yielded 0.075 g (10% of the theoretical) of ar-1-hydroxy-4-(aminoaceto)-tetralin hydrochloride, a white powder (turning pink in storage) with a m.p. of 235-237° (with decomposition and charring). It is soluble in water, methanol, and ethyl alcohol.

4.503 mg substance: 0.222 ml N_2 (20°, 771 mm). Found %: N 5.62. $C_{12}H_{15}O_2N \cdot HCl$. Computed %: N 5.79.

ar-1-Benzoylhydroxy-4-(diethylaminoaceto)-tetralin hydrochloride. 4 g of ar-1-benzoylhydroxy-4-bromacetotetralin and 20 ml of absolute benzene were placed in a three-necked flask, fitted with a reflux condenser and a stirrer. The suspension was stirred continuously and chilled externally while 1.6 g (2 moles) of freshly distilled diethylamine was added. Diethylamine hydrobromide was precipitated, the light-yellow reaction mixture turning reddish. Stirring was continued for 4.5 hours, and then the precipitate of diethylamine hydrobromide was quickly filtered out and washed with 6-8 ml of absolute benzene. This yielded 1.2 g (80% of the theoretical) of diethylamine hydrobromide, with a m.p. of 181-183°. The benzene was driven out of the mother liquor in vacuum, and the residue was distilled in ether. The ether solution was filtered, and an ether solution of hydrogen chloride was added to it, with constant stirring and chilling, until no more of the white curdled precipitate was thrown down. The precipitate adhered to the beaker walls and to the stirring rod; hence, the ether solution was decanted, and the beaker with the precipitate was placed in a vacuum desiccator. As the ether was exhausted from the adhering mass, the latter foamed and thickened. The resultant powder was triturated with anhydrous ethylacetate and then suction-filtered. This yielded 2.7 g (63% of the theoretical) of a colored powder with a m.p. of 172-177°. Recrystallization from absolute alcohol yielded 1.8 g (42% of the theoretical) of ar-1-benzoylhydroxy-4-(diethylaminoaceto)-tetralin hydrochloride as a white powder with a m.p. of 181-183.5° (with decomposition), soluble in ethyl alcohol and methanol, and insoluble in ether, acetone, or ethyl acetate. Its aqueous solution is readily hydrolyzed.

6.928 mg substance: 0.227 ml N_2 (19.5°, 733.5 mm). 8.659 mg substance: 3.009 mg AgCl. Found %: Cl 8.60; N 3.68. $C_{23}H_{27}O_3N \cdot HCl$. Computed %: N 3.49; Cl 8.84.

Picrate of ar-1-benzoylhydroxy-4-(diethylaminoaceto)-tetralin. 0.6 g of picric acid (1 mole) dissolved in 16 ml of alcohol, was added to 1 g of the unrefined base (m.p. 78-82°)*. The solution was allowed to stand for 24 hours, at the end of which time a red oil had formed. The oil was dissolved in absolute alcohol, and absolute ether was added to the alcoholic solution. The resulting yellow precipitate was recrystallized from absolute alcohol to which 1-2 drops of absolute ether had been added. The picrate of ar-1-benzoylhydroxy-4-(diethylaminoaceto)-tetralin consists of minute yellow needles with a m.p. of 122-123°, soluble in acetone, methanol, and ethyl alcohol, and in water upon heating.

4.902 mg substance: 0.418 ml N_2 (19°, 736.5 mm). Found %: N 9.23. $C_{28}H_{30}O_{10}N_4$. Computed %: N 9.43.

ar-1-Hydroxy-4-(diethylaminoaceto)-tetralin hydrochloride. 3 g of ar-1-benzoylhydroxy-4-(diethylaminoaceto)-tetralin hydrochloride, dissolved in 6 ml of methanol, was placed in a round-bottomed flask fitted with a reflux condenser. 9 ml of a 30% methanol solution of hydrogen chloride was added, and the whole was heated for 12 hours over a water bath. The alcohol was then driven off in vacuum. A 10% solution of ammonia was added to the residue (a red mass), and the mixture was extracted with ether until all of the substance had been dissolved in the ether. The ether solution was washed with water and desiccated with potash. The drying agent was filtered out and the solution was chilled and stirred while an ether solution of hydrogen chloride was added. A slightly colored amorphous precipitate was thrown down, which adhered to the walls of the beaker and to the stirring rod. The ether solution was poured off, and the beaker containing the precipitate was placed in a vacuum desiccator. Driving off the remainder of the ether yielded a friable powder, which was triturated with acetone, yielding 1.6 g (80% of the theoretical). Recrystallization from an acetone-methanol mixture yielded 1 g (60% of the theoretical) of ar-1-hydroxy-4-(diethylaminoaceto)-tetralin hydrochloride as a white powder with a m.p. of 203-205° (with decomposition), soluble in water, ethyl alcohol, and methanol, and insoluble in ether, acetone, or ethyl acetate.

6.799 mg substance: 0.275 ml N_2 (18°, 725.5 mm). 6.432 mg substance: 3.141 mg AgCl. 8.299 mg substance: 4.085 mg AgCl. Found %: Cl 12.04, 12.18; N 4.53. $C_{18}H_{23}O_2N \cdot HCl$. Computed %: Cl 11.93; N 4.7.

SUMMARY

1. ar-1-Benzoylhydroxy-4-(bromoaceto)-tetrahydronaphthalene has been synthesized by brominating ar-1-benzoylhydroxy-4-acetotetrahydronaphthalene.

2. ar-1-Benzoylhydroxy-4-(bromaceto)-tetrahydronaphthalene has been condensed with diethylamine, methylamine, benzylamine, and benzylmethylamine, the respective amino ketones being synthesized.

3. ar-1-Benzoylhydroxy(oxy)-4-(methylaminoaceto)- and ar-1-benzoylhydroxy-(oxy)-4-(aminoaceto)-tetralin have been synthesized by catalytically hydrogenating ar-1-benzoylhydroxy(-oxy)-4-(benzylaminoaceto)- and ar-1-benzoylhydroxy-(oxy)-4-benzylmethylaminoaceto)-tetralin, respectively.

LITERATURE CITED

[1] A.Akram and K.Desai, Chem.Zentr., 1940, 1, 3918.
[2] S.I.Sergievskaya and I.M.Lipovich, J.Gen.Chem. 17, 347 (1947).
[3] S.I.Sergievskaya and I.M.Lipovich, J.Gen.Chem. 18, 1400 (1948).
[4] I. Immediata and A.Day, J. org. Chem., 5, 512 (1940).
[5] S.I.Sergievskaya and L.M.Morozovskaya, J.Gen.Chem. 14, 1107 (1944).

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*Prepared by processing the hydrochloride with an aqueous solution of sodium bicarbonate.

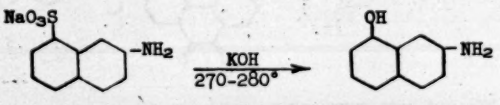
AZO DYES PRODUCED FROM 2,8-AMINONAPHTHOL AND ITS DERIVATIVES

I. AZO DYES FROM 2,8-AMINONAPHTHOL

V. V. Perekalin and N. M. Slabachevskaya

In a previously published paper, one of the present authors advanced a hypothesis to explain the nature of the reactions between aminonaphthol sulfo acids and diazo compounds [1]. The course taken by the azo coupling reactions of numerous sulfo acids of 1,5- and 2,8-aminonaphthol, forecast in accordance with this hypothesis, has been fully corroborated experimentally; in particular, we have been able to provide a theoretical explanation of why 1,5-aminonaphthol-7-sulfo acids (M acids) and 2,8-aminonaphthol-6-sulfo acids (gamma acids) fail to enter into a second coupling, and to provide experimental support therefor. The present paper deals with an investigation of the reaction of 2,8-aminonaphthol – the parent substance of the 2,8-aminonaphthol sulfo acids – with diazobenzene. In this research we had to determine the nature of the reaction of 2,8-aminonaphthol with diazo compounds as affected by the pH of the medium, i.e., to learn how a change in the pH affects the position at which the diazo constituent enters the aminonaphthol molecule, and also to solve the problem of whether azo dyes produced from 2,8-aminonaphthol (and, hence, whether 2,8-aminonaphthol itself) can form disazo dyes.

The 2,8-aminonaphthol was prepared by the alkaline fusion of the sodium salt of 2-naphthylamine-8-sulfonic acid by a method developed by L.N.Kononova (cf experimental section of this report).

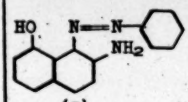
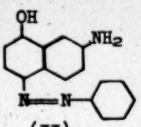


Reacting 2,8-aminonaphthol with 1 mole of diazobenzene at different values of the medium's pH yielded two dyes that proved to be monoazo dyes. One of them produced in glacial acetic acid (pH 1.0) and in hydrochloric acid (pH 1.25), which ordinarily cause coupling to occur at the amino group, was provisionally assigned the structure of an o-amino dye (I), while the other, produced chiefly in an alkaline medium (pH 11) which favors coupling at the hydroxy group, and in a medium of acetic acid and sodium acetate (pH 5.5) was assigned the structure of a p-hydroxy isomer (II) (Table 1). These dyes were identified by their melting points, the color of their solutions, and their solubility in different solvents; we also determined the positions of the longwave maxima in their absorption spectra.

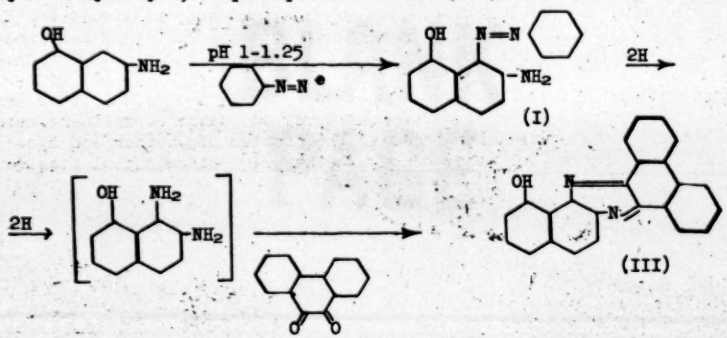
We then had to establish the structure of both isomers of the monoazo dye. The supposed o-aminoazo dye (I), which was synthesized without a trace of another isomer in glacial acetic acid, was reduced with zinc dust to diaminonaphthol in 80% acetic acid. We did not isolate this diamine, owing to its instability;

TABLE I

Yields of Monoazo Dyes as a Function of the pH of the Medium

No.	pH	Medium	Per cent yield		Total
			 (I)	 (II)	
1	1	Glacial acetic acid ...	39	0	39
2	1.25	Hydrochloric acid	26	21	48
3	5.5	10% Hydrochloric acid + an excess of sodium acetate	0	73	73
4	11	Alkaline	0	50	50

condensing it with a bisulfite derivative of phenanthraquinone yielded a phenazine dye – 8-hydroxy-1,2-naphthophenanthrazine (III):



This synthesis confirmed the assumption that the dye (I) was 1-benzeneazo-2,8-aminonaphthol, which is simultaneously an ortho amino and a peri-hydroxyazo dye. It turned out that this dye, which contains both an amino and a hydroxyl group, possesses a number of unusual properties: it is not detected in most of the reactions that are characteristic of these functional groups, viz.: the dye is not soluble in dilute alkalies, the position of the longwave maximum in its absorption spectrum is not affected when the measurements are made in alcoholic or alcoholic-alkaline media (cf. Figure and Table 2).

Hence, the hydroxyl group of the dye did not form a naphtholate, nor did the dye itself become an anion, since we know that the conversion of a neutral dye molecule into its anion is ordinarily accompanied by a shift in the longwave maximum of the absorption spectrum toward the longer wavelengths.

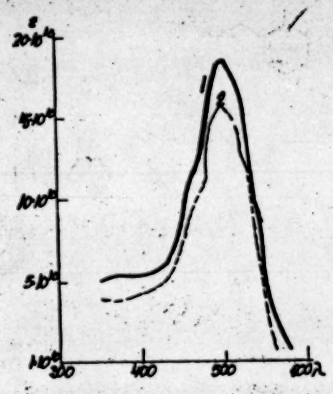
The color imparted to wool by this dye changed from orange-red to brown after chrome processing. This was evidence that the dye tends toward lake formation, and it may be supposed that the lake is formed from the hydroxyl and azo

groups, since we know the tendency of o-hydroxyazo dyes to form lakes [2] whereas o-aminoazo dyes are unable to form lakes, as has been demonstrated in the o-aminoazo dye synthesized from 1,5-aminonaphthol [3]. Thus, the hydrogen atom of the hydroxyl group lost its customary mobility, i.e., it was somehow blocked

TABLE 2

Position of Longwave Maxima in the Absorption Spectra of Dyes

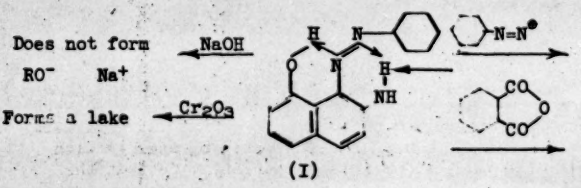
Dye	λ mμ	
	Ethyl alcohol	Ethyl alcohol + NaOH
1-Benzeneazo-2,8-aminonaphthol (I)	500	500
5-Benzeneazo-2,8-aminonaphthol (II)	505	520
5,7-Dibenzeneazo-2,8-aminonaphthol (VI)....	530	540



Absorption spectra of 1-benzeneazo-2,8-aminonaphthol (I)

1) In ethyl alcohol; 2) in a 1% alcoholic solution of caustic soda.

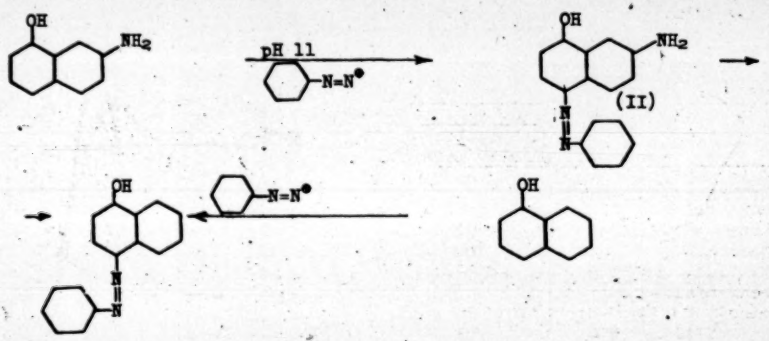
and at the same time replaced by a metal during the formation of the lake. As we have shown previously,* the insolubility of o-hydroxyazo dyes in dilute alkalies and their tendency to form lakes may be an indication of the presence of an intramolecular hydrogen bond [4]. It may therefore be assumed that here, too, a hydrogen bond is formed between the hydrogen of the hydroxyl group and one of the nitrogens in the azo group. The properties of the amino group are likewise somewhat unusual in this dye: in contrast to the amino group in the other isomer (II), it was not diazotized, and fusion (for 1-2 minutes) with phthalic anhydride did not result in the formation of a phthaloyl derivative. Phthaloylation under more severe conditions resulted in decomposition of the dye. After these two reactions were performed, the original dye was recovered quantitatively: its melting point and the color of its solutions in various solvents had not changed, nor did a test sample mixed with 1-benzeneazo-2,8-aminonaphthol exhibit any depression. Thus the amino group, like the hydroxyl group, had been deprived of most of its usual functions. This led us to suppose that one of the hydrogen atoms of the amino group formed a hydrogen bond with a nitrogen atom in the azo group.* The structure of the o-amino-peri-hydroxyazo dye (I) may, therefore, be represented by:



(I)

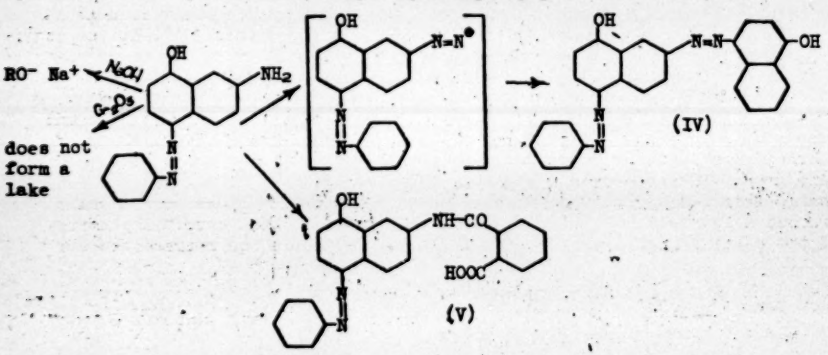
*In the terminology of classical theory these properties of the hydroxyl and amine groups are explained by a transition from the azoid form of the dye to its quinohydrazonium form. The concept of quinohydrazonium structure is found inadequate by now, so we have preferred the more modern concepts of a hydrogen bond [1,5,6].

The structure of the other isomer, the supposed p-hydroxyazo dye (II), was determined as follows: hydrogen was substituted for the amino group to yield a hydrazo dye, which was found to be identical with the p-hydroxyazo dye specially synthesized from 1-naphthol and diazobenzene:



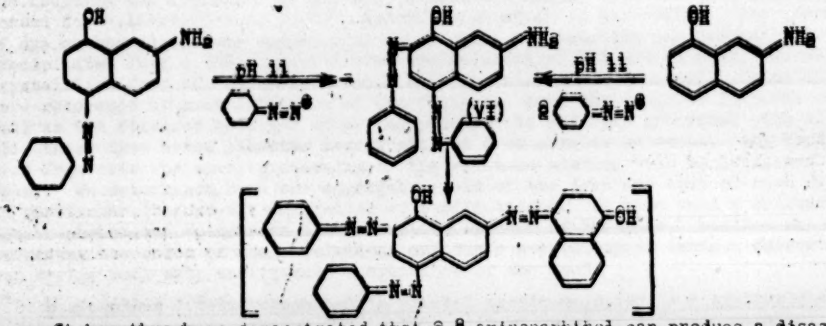
Hence there was no doubt about the structure of this isomer: it was 5-benzeneazo-2,8-aminonaphthol (II) and exhibited the reactions that are characteristic of the hydroxyl and amino groups. It was readily soluble in dilute alkalies, while the longwave maximum in its absorption spectrum was shifted from 505 to 520 mμ in the visible region (Table 2) when measurements were made in alcoholic and alcoholic-alkaline media; hence, the hydroxyl group formed a naphtholate. This dye did not form a lake, however.

The amino group was diazotized without difficulty: the diazo compound yielded a secondary disazo dye (IV) when it was coupled with 1-naphthol in an alkaline medium. Fusing it with phthalic anhydride resulted in the synthesis of a phthalcyl derivative - 5-benzeneazo-8-hydroxy-2-naphthylphthalamic acid, (V)



When we coupled 2,8-aminonaphthol in an alkaline or an acid medium, we were unable to secure the third isomer - an ortho hydroxyazo dye - from the alkali-insoluble residue, though its formation might have been expected by analogy with the coupling of 1-naphthol [7]. The reason for this, apparently, is that the velocity of coupling at the para position to the hydroxyl group (the α-position in naphthalene) was much higher than the velocity of coupling in the ortho position to it (the β-position in naphthalene). The final stage of our research

was an investigation of the ability of 2,8-aminonaphthol and of the dyes derived from it to form disazo dyes. All our efforts to synthesize a disazo dye from an o-aminazo dye - 1-benzeneazo-2,8-aminonaphthol - met with failure. Coupling with 1 mole of diazobenzene in alcohol with sodium ethylate present, or in 50% pyridine, yielded the original dye quantitatively (neither its melting point nor the color of its solutions changed, while a test sample mixed with chemically pure 1-benzeneazo-2,8-aminonaphthol exhibited no depression). The inertness of this dye to any reaction with another molecule of diazobenzene was due to the fact that the formation of a hydroxyl group diminished the activity of the hydrogen bond with respect to the aromatic ring. More precisely, the activity of the unshared electron pair in the hydroxyl group, the displacement of which within the ring is the basis for coupling, is diminished. When the second isomer - 5-benzeneazo-2,8-aminonaphthol (II) - was coupled with 1 mole of diazobenzene in an alkaline medium, we secured a 70% yield of a dye that proved to be a disazo dye. There were two places in the molecule of the original azo dye at which the second azo group could have entered: the ortho position to the amino group and the ortho position to the hydroxyl group. Inasmuch as no ortho aminoazo dye was formed with 2,8-aminonaphthol by coupling in an alkaline medium, and, in general, we know of no instances of coupling to an amino group in an alkaline medium, the only place where the second azo group could have entered was the ortho position to the hydroxyl group. Moreover, this disazo dye was diazotized and then coupled with 1-naphthol. If the second azo group had entered at the ortho position to the amino group, the latter would have lost its ability to be diazotized (cf. the properties of 1-benzeneazo-2,8-aminonaphthol). There was, therefore, no doubt that the disazo dye was an ortho, para hydroxyazo dye - 5,7-disbenzeneazo-2,8-aminonaphthol (VI). We synthesized the same dye by reacting 2,8-aminonaphthol with 2 moles of diazobenzene in an alkaline medium:



It has thus been demonstrated that 2,8-aminonaphthol can produce a disazo dye.

It should be noted that when the absorption spectra of this disazo dye were measured in alcoholic and alcoholic-alkaline media, the longwave maximum was shifted from 530 to 540 mμ in the visible region (Table 2). Hence, the hydroxyl group that was in the ortho position to the azo group constituted a naphtholate; we have shown that the position of the longwave maximum in the spectrum of an ortho hydroxyazo dye does not shift when shifting from an alcoholic to an alcoholic-alkaline medium, owing to the establishment of a hydrogen bond. This seeming contradiction may be explained as due to the fact that the increase in the acid properties (the mobility) of the hydrogen atom in the hydroxyl group, owing to the influence of the azo group in the para position to the hydroxyl group, outweighs the stabilization of this hydrogen atom, due to the formation of a hydrogen bond.

EXPERIMENTAL

1. Synthesis of 2,8-aminonaphthol. 38 g of solid KOH was melted in a nickel crucible, and 12.25 g (0.05 mole) of the finely powdered sodium 2-amino-8-sulfonate of naphthylamine [8,9] was gradually added, with intensive stirring, to the fused alkali at 240-250°. Fusion was continued for 7-9 minutes at 270-280°. The melt, a dark-brown homogeneous mass, was poured into 200 ml of cold water. After the mixture had cooled and been filtered, the alkaline solution was cautiously acidified with concentrated hydrochloric acid until all the sulfur dioxide had been driven off. The hot solution of 2,8-aminonaphthol hydrochloride was filtered and chilled. After the filtrate had been neutralized with a concentrated solution of sodium acetate, free 2,8-aminonaphthol settled out. The 2,8-aminonaphthol was cautiously dried (40-50°), being recovered as a light-gray powder. The yield was 40% of the theoretical; m.p. 155-156° (from water).

Experimental procedure used to synthesize the azo dyes. Chemically pure 2,8-aminonaphthol served as our raw material. We took 0.01 mole for each experiment, using it as a 0.1 N solution or suspension. In coupling the dyes, we again took 0.01 mole of each and prepared 0.1 N solutions. The pH of the medium was determined by potentiometric titration with the lamp potentiometer designed by the State Institute of Applied Chemistry. The diazo constituent used was diazobenzene, which was simplest to prepare and convenient for the subsequent analyses of the dyes. A decinormal solution of diazobenzene was prepared by diazotizing aniline by the customary method. The time required to add the diazo solution and for the ensuing coupling reaction was established in each individual case, depending upon the course of the coupling reaction. As a rule, the resultant isomers were isolated and purified by filtering the reaction mixture after the coupling was completed. If any precipitate was found, it was washed with water, heated for 5-10 minutes to 40-50°, and filtered after it had cooled. The residue of dye on the filter was washed with water until its reaction was neutral, reprecipitated from a 10% alcoholic-alkaline solution of 10% acetic acid, and recrystallized from the suitable organic solvent (alcohol or benzene). Other dyes were recovered by neutralization of the filtrate, both the original filtrate as well as the filtrate obtained after the precipitate had been processed with alkali, these dyes being likewise recrystallized from organic solvents. Any departures from this customary processing of the reaction mixture will be indicated below. We determined both the aggregate yield of the dyes and that of each dye in particular (before the completion of purification). We also used a Beckmann spectrophotometer to measure the absorption spectra of the dyes,* besides determining the color of their solutions and their solubility in various solvents and dyeing wool with acetic-acid suspensions of the dyes.

2. Coupling 2,8-aminonaphthol in glacial acetic acid (pH 1) – synthesis of 1-benzeneazo-2,8-aminonaphthol (I). 1.59 g (0.01 mole) of 2,8-aminonaphthol was dissolved in 100 ml of glacial acetic acid. 100 ml of a 0.1 N solution of diazobenzene (an equimolar quantity) was added to the solution of the dye at 10-15°, with constant stirring, during the course of 15 minutes; the first drop of the diazo solution turned the reaction mixture red-brown. The solution was stirred for an hour and then filtered; no precipitate was found in the filter. Twenty-four hours later the solution was refiltered, a dark-brown precipitate (0.1 g) of the dye being recovered. This dye proved to be the same as the dye recovered from the acetic-acid filtrate. The acetic-acid filtrate was diluted with four times its volume of water and then neutralized with a 10% solution of caustic soda; this yielded 0.9 g of the dye. The aggregate yield was 1 g (39% of the theoretical). The dye recovered from the acetic-acid filtrate was rubbed twice with 10 ml of a 10% solution of caustic soda, diluted to 100 ml with water,

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*The absorption spectra were measured by N. N. Pribytkova to whom we are indebted.

heated over a water bath for 10-15 minutes, and filtered after it had cooled. No perceptible quantities of the dye were recovered from the alkaline filtrates, which were fairly red. The dye that was insoluble in alkali was dissolved in 100 ml of 10% alcoholic alkali at 40-50°. The filtrate was acidified with 150 ml of 1% hydrochloric acid, yielding an orange-red flocculent precipitate. Recrystallization from 50% aqueous alcohol yielded the dye as dark-red, bronze-colored platelets; m.p. 176°. The dye is freely soluble in ethyl alcohol, glacial acetic acid, and acetone; less so in benzene, toluene, or xylene. See Table 3 for the color of its solutions and for its solubility.

0.1170 g substance: 0.3150 g CO_2; 0.0312 g H_2O. 0.0697 g substance: 9.8 ml N_2 (20°, 749 mm). Found %: C 73.04; H 5.09; N 16.16. $C_{16}H_{13}ON_3$. Computed %: C 73.0; H 4.94; N 15.97.

TABLE 3

Color of Solutions and Solubility

Dye	Solutions		
	10% NaOH	10% alcoholic NaOH	96% H_2SO_4
8-Hydroxy-1,2-naphthophenanthrazine (III)	Insoluble	Brown-red solution	Intensely blue solution

3. Determination of the structure of the supposed 1-benzeneazo-2,8-aminonaphthol (I). a) Reduction of the dye. 2.63 g (0.01 mole) of the dye was dissolved in 50 ml of 80% acetic acid at 50-60°. Zinc dust was added to the red solution, with vigorous stirring, until the color of the solution vanished. After the solution had cooled and been filtered, the diaminonaphthol was not isolated from the acetic-acid solution, but immediately condensed with a bisulfite solution of phenanthraquinone.

b) Condensation of diaminonaphthol with phenanthraquinone — synthesis of 8-hydroxy-1,2-naphthophenanthrazine (III). 2.08 g (0.01 mole) of phenanthraquinone was heated in 60 ml of a 37% bisulfite solution over a water bath until it dissolved and was then poured into the acetic-acid solution of the diaminonaphthol; then the mixture was boiled for 15 minutes, a copious flocculent, bright-yellow precipitate slowly settling out of the solution. M.p. 300° (from chlorobenzene). 8-Hydroxy-1,2-naphthophenanthrazine consists of minute yellow crystals, slightly soluble in ethyl alcohol or acetone, more soluble in benzene.

0.1286 g substance; 9.0 ml N_2 (16°, 756 mm). Found %: N 8.22. $C_{24}H_{14}ON_2$. Computed %: N 8.09.

4. Attempt to diazotize 1-benzeneazo-2,8-aminonaphthol (I). 0.47 g (0.002 mole) of the dye was mixed with 0.6 ml of 37% hydrochloric acid and then diluted with 10 ml of water. A solution of 0.15 g of sodium nitrite in 2 ml of water was added to the resulting suspension during the course of 5 minutes at 0-5°, with constant stirring. Four hours later, the colorless filtrate, neutralized with a 10% solution of sodium acetate until its reaction was slightly acid with Congo red, was divided into two parts. One part was added to an alkaline solution of 1-naphthol; the color of the solution did not change; after stirring for two hours the original 1-naphthol was recovered quantitatively. Cotton, naphthalized with naphthol AC, was immersed in the other part of the filtrate; the fabric did not change color after 4 hours had passed. The deposit recovered after the suspension had been filtered had m.p. of 172°; a test sample mixed with 1-benzeneazo-2,8-aminonaphthol (m.p. 176°) had a m.p. of 174°. The color of solutions of the deposit and of the original 1-benzeneazo-2,8-aminonaphthol in 96% sulfuric

acid, 37% hydrochloric acid, 100% acetic acid, and ethyl alcohol were identical.

5. Attempt to phthaloylate 1-benzeneazo-2,8-aminonaphthol (I). 0.47 g (0.002 mole) of the dye was rubbed with 0.3 g of phthalic anhydride and cautiously heated for 1-2 minutes until the mixture melted. Then the melt was treated with a 10% solution of soda and filtered; the pink filtrate was acidified with 37% hydrochloric acid, causing a minute precipitate to settle out. The residue obtained after filtering the suspension had a m.p. of 171°; a test sample mixed with the original 1-benzeneazo-2,8-aminonaphthol fused at 173°. The color of solutions of the residue and of the 1-benzeneazo-2,8-aminonaphthol were identical.

6. Coupling 2,8-aminonaphthol in a hydrochloric acid medium, (pH 1.5) - synthesis of 1-benzeneazo-2,8-aminonaphthol (I) and 5-benzeneazo-2,8-aminonaphthol (II). 1.59 g 2,8-aminonaphthol, dissolved in 10 ml 10% hydrochlorid acid, diluted to 100 ml with water, was combined with 100 ml of 0.1 N diazobenzene solution, which was added during the course of two hours, after which the mixture was set aside to stand overnight; the next day the fine-grained precipitate was filtered out. The yield of the dye was 2.5 g (48% of the theoretical). The faintly colored filtrate did not contain perceptible quantities of the dye. The precipitate was processed with a 10% solution of caustic soda as specified in Section 2, and filtered. The residue on the filter, totaling 1.4 g (56% of the total of the mixture), was identical with the 1-benzeneazo-2,8-aminonaphthol; its m.p. was 170°, and the color of their solutions and the solubilities of the two dyes were the same. Nor did a mixed fusion test of the two exhibit any depression of the melting point. The intensely red filtrate was acidified with 10% acetic acid, yielding 1.1 g of the dye (44% of the total dye mixture). This dye was reprecipitated from an alkaline solution of acetic acid and recrystallized from benzene. The m.p. (174°) and the color of the solutions of this dye were the same as those of 5-benzeneazo-2,8-aminonaphthol (synthesized in an alkaline medium). A mixed fusion sample of the two dyes had a m.p. of 174°.

7. Coupling 2,8-aminonaphthol in sodium acetate (pH 5.5) - synthesis of 5-benzeneazo-2,8-aminonaphthol (II). 1.59 g of 2,8-aminonaphthol was dissolved in 10 ml of 10% hydrochloric acid and then diluted with water to 100 ml; 10 g of sodium acetate was then added to the solution, and the resulting suspension was combined for 4 hours with 100 ml of a 0.1 N solution of diazobenzene. After the coupling reaction was over, the dark-brown flocculent precipitate was filtered out. The yield was 3.8 g (73% of the theoretical). The dye was readily dissolved in 10% caustic soda and processed as described below in Section 8. This dye proved to be the same as 5-benzeneazo-2,8-aminonaphthol (II).

8. Coupling 2,8-aminonaphthol in an alkaline medium (pH 11) - synthesis of 5-benzeneazo-2,8-aminonaphthol (II). 1.59 g of 2,8-aminonaphthol was dissolved in 10 ml of 10% caustic soda (1 mole excess) and diluted with water to 100 ml; then 100 ml of a 0.1 N solution of diazobenzene was added at 10-15°, with constant stirring, during the course of 15 minutes. The solution was stirred for another 30 minutes after all the diazobenzene had been added and then filtered; a minute precipitate was found on the filter. 4.3 g of a dye (81% of the theoretical) was recovered from the intensely red filtrate by acidulating it with 10% acetic acid. This dye was twice reprecipitated from a 10% alkaline solution with 10% acetic acid; its m.p. was 174° after recrystallization from benzene. The dye consisted of dark-brown, bronze-colored crystals, which were freely soluble in ethyl alcohol, glacial acetic acid, acetone, and benzene; it was less soluble in xylene or toluene. A test sample mixed with 1-benzeneazo-2,8-aminonaphthol (m.p. 176°) had a m.p. of 154°. See Table 4 for the color of its solutions and its solubilities.

0.1417 g substance: 0.3795 g CO_2; 0.0625 g H_2O. 0.1360 g substance: 19.2 ml N_2 (20°, 748 mm). Found %: C 73.27; H 4.93; N 16.19. $C_{16}H_{13}O_3N_3$. Computed %: C 73.0; H 4.94; N 15.97.

TABLE 4

Color of Solutions and Solubility

No.	Dye	Solutions			
		10% NaOH	95% H_2SO_4	37% HCl	100% CH_3COOH
1	1-Benzeneazo-2,8-aminonaphthol (I) ..	Insoluble	Intensely blue solution	When heated, red-purple solution	Brown solution
2	5-Benzeneazo-2,8-aminonaphthol (II)..	Intensely red solution	Red-purple solution	Red-purple solution	Brown solution
3	5,7-Disbenzeneazo-2,8-aminonaphthol (VI)	Insoluble	Purple-blue solution	When heated, purple-blue solution	Brown-red solution

The precipitate on the filter was twice treated with a 10% solution of caustic soda, reprecipitated from a 10% solution of alcoholic alkali with concentrated hydrochloric acid, and recrystallized from chlorobenzene; m.p. 232°. The color of the solutions and the solubility of this dye were the same as those of 5,7-disbenzeneazo-2,8-aminonaphthol (VI). A mixed test sample of the two dyes exhibited no depression (m.p. 232°).

9. Determination of the structure of the supposed 5-benzeneazo-2,8-aminonaphthol (II). Substituting an amino group for hydrogen. 0.65 g of the dye (0.025 mole) was dissolved by heating it in 10 ml of absolute ethyl alcohol. After the solution had cooled, 0.49 g of 95% sulfuric acid was added and 0.22 g of sodium nitrite was cautiously added. Then the solution was heated over a water bath (the vigorous evolution of gas bubbles was observed), allowed to cool, and filtered. When water was added to the alcohol solution a brown-red dye was precipitated, which had a m.p. of 203° after reprecipitation with 10% hydrochloric acid from a 10% alkali solution and recrystallization from benzene. A test sample mixed with specially synthesized 4-benzeneazo-1-naphthol (m.p. 205°) had a m.p. of 204°.

10. Diazotization of 5-benzeneazo-2,8-aminonaphthol and synthesis of 1-(4-naphthol)-azo-5-benzeneazo-2,8-aminonaphthol (IV). 0.43 g (0.002 mole) of the dye was mixed with 3 ml of 37% hydrochloric acid and diluted with 3 ml of water, and a solution of nitrite in 3 ml of water was added to the resultant suspension drop by drop at 0-5°, with constant stirring. The solution was filtered four hours later; no precipitate was discovered on the filter. The filtrate was neutralized with a 10% solution of sodium acetate and combined with a solution of 0.28 g of 1-naphthol in 10 ml of a 10% solution of sodium hydroxide. Acidifying the solution 2 hours later with 10% hydrochloric acid yielded a dye. M.p. 110° (with decomposition). See Table 5 for the color of its solutions.

TABLE 5

Color of Solutions

Dye	Solutions			
	10% NaOH	96% H_2SO_4	37% HCl	100% CH_3COOH
1-(4'-Naphthol)-azo-5-benzeneazo-2,8-aminonaphthol (IV)	Red solution	Green solution	When heated, red-purple color	Red-brown solution

11. Phthaloylation of 5-benzeneazo-2,8-aminonaphthol – synthesis of 5-benzeneazo-8-hydroxy-2-naphthylphthalâmic acid (V). 0.43 g (0.002 mole) of the dye was rubbed with 0.3 g of phthalic anhydride (equimolar quantity) and then cautiously heated for 1-2 minutes until the mixture melted. Then the melt was gently heated and dissolved in 10 ml of a 10% soda solution; filtration of the intensely green solution and acidulation with concentrated hydrochloric acid yielded a precipitate of the dye. Reprecipitation from a soda solution by hydrochloric acid yielded a brown-red dye with a m.p. of 197°. Yield 0.78 g.

Synthesis of Disazo Dyes

12. Coupling of 5-benzeneazo-2,8-aminonaphthol in an alkaline medium (pH 11) – synthesis of 5,7-disbenzeneazo-2,8-aminonaphthol (VI). 2.63 g (0.01 mole of the dye was dissolved in 12 ml of a 10% solution of caustic soda, diluted with water to 100 ml, and combined with 100 ml of a 0.1 N solution of diazobenzene, which was added during the course of 2 hours at 0-5°, with constant stirring, after which the coupling reaction continued for 4 hours. Then the dark-brown precipitate was filtered out; this yielded 1.27 g of a dye (71% of the theoretical). 0.12 g of the original dye was recovered from the filtrate by acidulating it with a 10% solution of acetic acid. The precipitate was triturated with 5 ml of a 10% solution of caustic soda, diluted with water to 100 ml, and heated for 10-15 minutes over a water bath. The solution was allowed to cool and then filtered. Acidulation of the filtrate with 10% acetic acid yielded 0.3 g of the original dye.

The alkali-insoluble precipitate on the filter was washed with water until its reaction was neutral, mixed with 50 ml of a 1% solution of hydrochloric acid, and heated to 40-50° for 10-15 minutes. Then the precipitated dye was reprecipitated by concentrated hydrochloric acid from a 10% solution of alcoholic alkali. The dye, black powder with a m.p. of 232° (from chlorobenzene), was freely soluble in acetone, less so in toluene or benzene.

0.0856 g substance: 14.6 ml N_2 (21°, 738 mm); 0.0692 g substance: 11.6 ml N_2 (20°, 756 mm). Found %: N 19.01, 19.31.
$C_{27}H_{17}ON_5$. Computed %: N 19.17.

13. Coupling 2,8-aminonaphthol with 2 moles of diazobenzene in an alkaline medium – synthesis of 5,7-disbenzeneazo-2,8-aminonaphthol (VI). 1.59 g (0.01 mole) of the aminonaphthol was dissolved in 16 ml of a 10% caustic soda solution, diluted with water to 100 ml, and combined with 200 ml of a 0.1 N solution of diazobenzene at 0-5°, with constant stirring. The diazobenzene solution was added in the course of 2 hours, after which the coupling reaction continued for another 2 hours. Then the suspension was filtered out and a minute quantity of 5-benzeneazo-2,8-aminonaphthol was recovered from the intensely red filtrate by acidulating it with a 10% solution of acetic acid. The dye precipitate was processed in the usual manner by heating it with a 10% solution of caustic soda; upon cooling, the solution was filtered, an alkali-insoluble precipitate remaining on the filter. Acidulating the filtrate with 10% acetic acid yielded 0.4 g of 5-benzeneazo-2,8-aminonaphthol. The yield of the alkali-insoluble dye was 1 g (28.5% of the theoretical), based on the diazo dye. M.p. 232° (from chlorobenzene).

A test sample, mixed with 5,7-disbenzeneazo-2,8-aminonaphthol (VI, 232°), exhibited no depression, while the solution colors and the solubilities of the synthesized dye and of dye (VI) were completely identical.

14. Attempt to synthesize a diazo dye from 1-benzeneazo-2,8-aminonaphthol with sodium ethylate in an alcohol medium. 0.26 g (0.001 mole) of the dye was

dissolved in 25 ml of ethyl alcohol, in which 0.23 g of metallic sodium (0.01 mole) had been dissolved, and combined for 2 hours at 5-10° with 10 ml of a 0.1 N solution of diazobenzene. The solution was filtered 24 hours later, yielding 0.2 g of a dye. Acidulating the filtrate with 50 ml of 1% hydrochloric acid yielded 0.05 g of a dye. Both residues had m.p. of 176° after recrystallization from 50% aqueous alcohol. Their test samples exhibited no depression when mixed with the original 1-benzeneazo-2,8-aminonaphthol.

15. Attempt to synthesize a disazo dye from 1-benzeneazo-2,8-aminonaphthol in 50% aqueous pyridine. 0.26 g (0.001 mole) of the dye was dissolved in 10 ml of pyridine and then diluted with 10 ml of water; the solution was combined with 10 ml of a 0.1 N solution of diazobenzene at 0-5° for 4 hours. Then the reaction mixture was filtered, yielding 0.1 g of a precipitate; another 0.15 g of a dye was recovered from the water-pyridine filtrate by acidulating it with hydrochloric acid and diluting it with 10 ml of water. Both precipitates had a m.p. of 176° (from 50% aqueous alcohol). Their test samples exhibited no depression when mixed with the original dye.

SUMMARY

1. It has been shown that coupling 2,8-aminonaphthol with 1 mole of diazobenzene yields two monoazo dyes: an o-amino-peri-hydroxyazo dye (1-benzeneazo-2,8-aminonaphthol) and a p-hydroxyazo dye (5-benzeneazo-2,8-aminonaphthol).

2. The unusual properties of the o-amino-peri-hydroxyazo dye, in particular the inability of this dye to enter into diazo coupling, may be explained by the formation of two intramolecular hydrogen bonds between the hydrogen atoms of the amino and hydroxyl groups and the nitrogen atoms of the azo group.

3. It has been found that 2,8-aminonaphthol and the 5-benzeneazo-2,8-aminonaphthol synthesized from it can form a disazo dye: 5,7-disbenzeneazo-2,8-aminonaphthol.

4. Changing the pH of the medium (neutral and alkaline) does not affect the position of the longwave maximum of the absorption spectrum of an o-amino-peri-hydroxyazo dye.

LITERATURE CITED

[1] V.V.Perekalin, J.Gen.Chem. 17, 1788 (1947).

[2] Baudisch, Ber., 50, 330, 333 (1917).

[3] V.V.Perekalin, J.Gen.Chem. 15, 446 (1945).

[4] V.V.Perekalin, J.Gen.Chem. 21, 129 (1951).*

[5] B.A.Porai-Koshits and L.S.Efros, J.Gen.Chem. 18, 929 (1948).

[6] V.N.Ufimtsev, J.Gen.Chem. 13, 520 (1943).

[7] Charier, Gazz. chim. Ital., 44, 1, 607.

[8] German Patent 20,760; Friedl., 1, 419.

[9] German Patent 29,084; Friedl., 1, 421.

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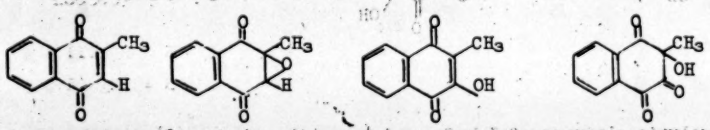
* See CB translation p. 141 ff.

OXIDATIVE AND OXIDATIVE-HYDROLYTIC TRANSFORMATIONS OF ORGANIC MOLECULES

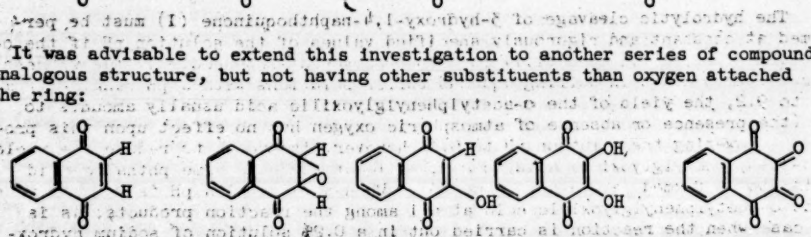
XIV. THE HYDROLYTIC CLEAVAGE OF 3-HYDROXY-1,4-NAPHTHOQUINONE*

L. A. Shchukina, A. S. Khokhlov, and M. M. Shemyakin

In order to discover the relationships existing between the degree of oxidation of molecules and the ability of their carbon bonds to be cleaved by hydrolyzing agents, we began an investigation some years ago of the conditions governing the hydrolytic and oxidative-hydrolytic cleavage of cyclic systems, and the nature of this cleavage in the following series of 2-methyl-substituted carbocyclic compounds, which are the products of a progressive oxidation of the molecule of 2-methyl-1,4-naphthoquinone [1-5]:



It was advisable to extend this investigation to another series of compounds of analogous structure, but not having other substituents than oxygen attached to the ring:

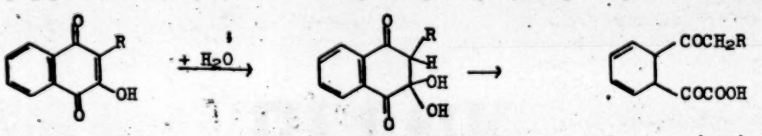


We chose the latter series of substances, which represents all the stages of oxidation of the molecule of the original 1,4-naphthoquinone, because it enabled us to shed clearer light upon the extent of the influence of oxygen-containing substituents upon the hydrolytic cleavage of carbon bonds in carbocyclic compounds. Comparison of our results with those previously described for the similarly constructed 2-methyl-substituted compounds [1-5] also enables us to solve the problem of whether the hydrolytic and oxidative-hydrolytic transformations of these carbocyclic compounds depended on the replacement of the hydrogen atom at the 2-position in their molecules by a methyl group. We set as our goals in this investigation: determining the conditions under which the carbon bonds are cleaved in the compounds specified, the nature of the resulting cleavage products, and the course of the secondary reactions that often occur during processes of this type. The results of our study of the oxidative-hydrolytic

*Report XII on the hydrolytic cleavage of carbon bonds.

transformations of 1,4-naphthoquinone have already been set forth in one of our previous reports [1].* The material on the hydrolytic cleavage of 3-hydroxy-1,4-naphthoquinone is set forth in the present paper. As for the hydrolytic and oxidative-hydrolytic transformations of the oxide of 1,4-naphthoquinone, 2,3-dihydroxy-1,4-naphthoquinone, and 1,2,3,4-tetraketo-1,2,3,4-tetrahydronaphthalene, we shall deal with these reactions in detail in two of our subsequent reports.

We might have expected that 3-hydroxy-1,4-naphthoquinone (I), like the previously investigated 2-methyl-3-hydroxy-1,4-naphthoquinone (II) [2], would undergo merely hydrolytic cleavage, without requiring that an oxidizing agent also be present, and, as we saw it, this process ought to take place under practically identical conditions for both quinones, inasmuch as the methyl group is unable to exert any strong influence upon the polarization of the carbon bonds and hence cannot affect their cleavability by hydrolytic agents. This assumption proved to be correct. It was found that both of these quinones are cleaved by boiling for a long time in aqueous buffer solutions with a pH somewhat above 7, yielding primary cleavage products of analogous structure, to wit: o-acetylphenylglyoxilic acid (III) from 3-hydroxy-1,4-naphthoquinone (I) (vide infra) and o-propionylphenylglyoxilic acid (IV) from 2-methyl-3-hydroxy-1,4-naphthoquinone (II) [2];



R = H (I)
R = CH_3 (II)

R = H (III)
R = CH_3 (IV)

The hydrolytic cleavage of 3-hydroxy-1,4-naphthoquinone (I) must be performed at constant and rigorously specified values of the solution pH if the o-acetylphenylglyoxylic acid (III) is to be recovered unchanged. If the process is run for 48 hours in boiling aqueous buffer solutions with a pH ranging from 7.3 to 9.2, the yield of the o-acetylphenylglyoxilic acid usually amounts to 30% (the presence or absence of atmospheric oxygen has no effect upon this process). Lowering the solution pH to 6.8, however, is enough to reduce the yield of o-acetylphenylglyoxilic acid to 22%, while at the same time phthalic acid begins to be formed (a yield of some 5%). When the solution pH is 4.3, there is no o-acetylphenylglyoxilic acid at all among the reaction products, as is the case when the reaction is carried out in a 0.2% solution of sodium hydroxide. The recovery of the o-acetylphenylglyoxilic acid from the reaction solution and its subsequent purification involved no significant difficulties (cf the experimental section). It crystallizes freely from small quantities of water as white crystals (m.p. 72°), containing one molecule of water of crystallization; the latter may be readily eliminated by heating the substance in vacuum. The anhydrous acid fuses at 123-124°. Recrystallization from water again turns it into the original monohydrate. Inasmuch as the acid we had synthesized was not described in the literature, we had to make a special study of its structure. The investigations carried out in this connection left no room for doubt that the synthesized compound actually was o-acetylphenylglyoxilic acid (III). The anhydrous acid with a m.p. of 123-124° had the empirical formula of $C_{10}H_8O_4$. This acid possesses two active hydrogen atoms (determined by the A.P.Terentyev method). As will be shown below, one of these hydrogen atoms belongs to the

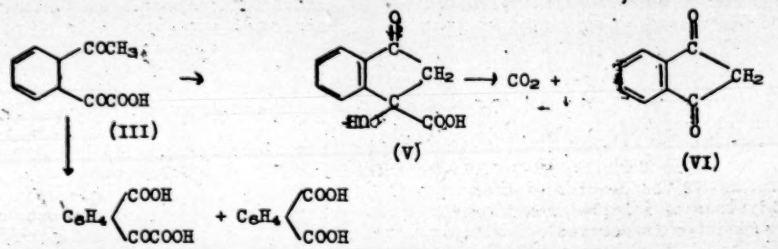
*By way of supplementing the previously published data, we should merely like to note the oxidative-hydrolytic transformation of 1,4-naphthoquinone effected by boiling it in an aqueous alkaline solution in the presence of atmospheric oxygen results in the formation of phthalonic acid as well as phthalic acid (cf experimental part below).

carboxylic group, while the other belongs to the $-COCH_3$ group constituting part of this acid. The monohydrate with a m.p. of 72° has the empirical formula of $C_{10}H_8O_4 \cdot H_2O$. It contains four active hydrogen atoms. Inasmuch as this compound can be readily prepared in the pure state, we used it in our subsequent research. The substance with a m.p. of 72° contains one carboxyl group, as can be determined by titration with an alkali solution. This substance readily forms a silver salt, $(C_9H_7O_2)COOAg$, which is converted to the methyl ester, with a m.p. of 92°, by the action of methyl iodide.* The analysis data of this ester are satisfied by the formula $(C_9H_7O_2)COOCH_3$. Its molecule contains one active hydrogen atom. Boiling the ester with a 10% aqueous solution of sulfuric acid yields the original acid with a m.p. of 72°. The latter forms, in addition to the monomethyl ester, a monosemicarbazone, with a temp. decomp. of 158-160°, which crystallizes with one molecule of water. The composition of this semicarbazone is that of a compound with the formula $C_9H_7O(COOH)(C{=}NNHCONH_2) \cdot H_2O$. When the substance with a m.p. of 72° is reacted with an alkaline solution of hypoiodite under the usual conditions of a Lieben reaction, only traces of iodoform are found. But when this reaction is carried out without heating, substituting a soda solution for the solution of caustic alkali, we manage to secure more than 30% of iodoform, proving that the compound in question contains the $-COCH_3$ group. On the other hand, when the compound in question is cautiously oxidized with chromic acid in the presence of sulfuric acid, small amounts of phthalonic acid may be recovered, in addition to appreciable amounts of phthalic acid. This indicates that the substance with a m.p. of 72° is a benzene derivative, containing, in addition to the $-COCH_3$ group, the $-COCOOH$ group, which is in the ortho position to the former.

The reactions described above enable us to establish the position as well as the nature of all the substituents in the molecule of the substance with a m.p. of 72° we had isolated. More especially, the presence of the $-COCH_3$ group made it impossible to assign this compound the structure of a bicyclic α-hydroxy acid (V), which would simultaneously explain the presence of one active hydrogen atom in the methyl ester with a m.p. of 92°, of two active hydrogen atoms in the anhydrous acid with a m.p. of 123-124°, and of four active hydrogen atoms in the latter's monohydrate with a m.p. of 72°, inasmuch as we know [2,7] that one hydrogen atom of a methyl or methylene group attached to the carbonyl group is also found, as a rule, in the determination of active hydrogen atoms by the A.P.Terentyev method. Thus, the properties and the conversions of the substance with a m.p. of 72°, as well as the conditions of its formation from 3-hydroxy-1,4-naphthoquinone, are adequate testimony that this substance is o-acetylphenylglyoxilic acid (III). It should be borne in mind that the oxidation of this acid which chromic acid, described above, ordinarily results in the formation of appreciable quantities of indandione-1,3 (VI), in addition to the phthalic and phthalonic acids. The indandione was identified as the preparation we had synthesized by a method described earlier [8]. Moreover, it was identified in the respective benzal derivative [8], as well as in the so-called bindone [8]. The conversion of o-acetylphenylglyoxilic acid into indandione-1,3 under such mild conditions indicates that this acid apparently has a very pronounced tendency to close a ring, forming the isomeric cyclic α-hydroxy acid (V), which is then oxidized by the chromic acid to the end product indandione-1,3 (VI) (at the same time splitting out the carboxyl group as CO_2). This reaction may serve as supplementary proof of the correctness of the formula (III), proposed for the acid

*While carrying out this reaction we discovered a highly singular and, apparently, hitherto unobserved phenomenon. We found that when the methyl iodide was added to the anhydrous precipitate of the silver salt, the latter dissolved nearly instantaneously, a precipitate of silver iodide beginning to settle out of the initially wholly transparent solution after 10 to 15 seconds had elapsed. Obviously, an unstable coordination compound was formed at first, the addition product of methyl iodide and the silver salt, which is then decomposed into silver iodide and the methyl ester of o-acetylphenylglyoxilic acid.

with a m.p. of 72° we had isolated, inasmuch as it is a matter of common knowledge by now that substances of this sort tend to be converted into cyclic α-hydroxy acids, which are readily decarboxylated oxidatively to the respective carbonyl compounds [2,10-12]. The oxidation of o-acetylphenylglyoxilic acid with chromic acid is shown in the subjoined diagram:



Comparison of our results with the data obtained previously indicates that the hydrolytic cleavage of 3-hydroxy-1,4-naphthoquinone and of 2-methyl-3-hydroxy-1,4-naphthoquinone takes place under practically identical conditions, resulting in compounds of analogous structure. It follows, therefore, that substituting a methyl group for the hydrogen atom at the 2 position in the hydroxynaphthoquinone molecule has no significant effect upon the cleavage of its cyclic groups.

EXPERIMENTAL *

1. Hydrolytic Cleavage of 3-Hydroxy-1,4-naphthoquinone

a) In a buffer solution of pH 7.3. 1.5 liters of a phosphate buffer solution (pH 7.3; buffer capacity 2/15 mole) was placed in a round-bottomed flask, fitted with a reflux condenser and a tube extending to the bottom of the flask, through which a gentle current of air was passed during the experiment in order to ensure uniform boiling. 3 g of 3-hydroxy-1,4-naphthoquinone was added to the boiling solution.** The reaction solution turned dark red, the color persisting to the end of the reaction. Boiling was continued for 48 hours, after which the solution was cooled and acidulated with 30% sulfuric acid until its reaction was acid with Congo red, the resultant precipitate being filtered out and washed with a small quantity of water. This yielded 1.3 g of 3-hydroxy-1,4-naphthoquinone with a m.p. of 190-191° (from alcohol). The reaction solution was evaporated in vacuum at 50° to a volume of some 300 ml and chilled, another 0.2 g of 3-hydroxy-1,4-naphthoquinone with a m.p. of 190-191° (from alcohol) that was precipitated being filtered out. The filtrate was extracted with ether four times. The ether solution was boiled with activated charcoal, and the ether was driven off. The residue was o-acetylphenylglyoxilic acid as a thick, light-yellow oil, nearly all of which crystallizedwhen rubbed with 1-2 drops of water. 1-2 ml of ether was added to the synthesized substance and the precipitate was filtered out. This yielded 1.1 g (30%) of o-acetylphenylglyoxilic acid monohydrate, with a m.p. of 72° (from water). See Experiment 2, below, for its properties and the determination of its structure.

b) In a buffer solution of pH 9.17. When 3 g of 3-hydroxy-1,4-naphthoquinone was boiled in a phosphate buffer solution with a pH of 9.17 under the conditions specified above, the reaction was the same as described under Experiment

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*The analytical portion of this research was performed with the assistance of E. A. Ignatyeva, to whom we are profoundly thankful.

**3-Hydroxy-1,4-naphthoquinone was synthesized from 1-amino-2-naphthol-4-sulfonic acid [13]. It fuses at 191° (from methanol).

1, a. The yield was 1.1 g (30%) of o-acetylphenylglyoxilic acid.

c) In a buffer solution of pH 7.02. When 3 g of 3-hydroxy-1,4-naphthoquinone was boiled in a phosphate buffer solution with a pH of 7.02 under the conditions used for Experiment 1,a, we secured a small quantity of a black, highly tarred substance that did not dissolve in an alkali solution. It was filtered out (weight 0.1 g), and acidulation of the reaction solution yielded 2.0 g of the original 3-hydroxy-1,4-naphthoquinone and 0.6 g (16%) of o-acetylphenylglyoxilic acid.

d) In a buffer solution of pH 6.82. Boiling 3 g of 3-hydroxy-1,4-naphthoquinone in a phosphate buffer solution with a pH of 6.82 yielded 0.3 g of a black substance that was insoluble in an alkali solution. The unreacted 3-hydroxy-1,4-naphthoquinone totaled 0.9 g. After the original quinone had been filtered out, the mother liquor was evaporated to a volume of some 300 ml and extracted four times with ether. The mixture of o-acetylphenylglyoxilic and phthalic acids left after the ether had been driven off was separated by heating it with benzene, in which phthalic acid is practically insoluble. This yielded 0.15 g (5%) of phthalic acid and 0.8 g (22%) of o-acetylphenylglyoxilic acid.

e) In a buffer solution of pH 7.4 with atmospheric oxygen excluded. This experiment was carried out in a wide-necked flask, fitted with a reflux condenser, a dropping funnel, and a tube extending to the bottom of the flask, through which hydrogen was passed during the experiment. The flask stopper had a hole through which there tightly passed a glass rod, terminating in a hook, from which there was hung a container with 3 g of 3-hydroxy-1,4-naphthoquinone before the beginning of the experiment. 1.5 liters of a phosphate buffer solution (pH 7.4; buffer capacity 2/15 mole) was placed in the flask. The system was made airtight and then filled with hydrogen. The latter was first purified by passing it through alkaline solutions of permanganate and pyrogallol and then over a bed of copper heated to 300-400°. The hydrogen passed out of the system via the reflux condenser, connected to two Tishchenko bottles containing an alkaline solution of pyrogallol. It took 4 hours to drive out the air during which time the buffer solution in the flask was boiled continuously to drive out the last trace of air dissolved in it. After the four hours were over, the container with the 3-hydroxy-1,4-naphthoquinone was immersed in the solution, and boiling was continued for 48 hours, the flow of hydrogen continuing throughout. After this boiling, the solution was cooled in a current of hydrogen and then acidulated with a previously measured quantity of 50% sulfuric acid, the latter being added through the dropping funnel. The subsequent analysis of the solution is the same as in Experiment 1, a. This yielded 1.4 g (47%) of the original 3-hydroxy-1,4-naphthoquinone and 1.1 g (30%) of the o-acetylphenylglyoxilic acid with a m.p. of 72°.

2. Proof of the Structure and Properties of o-Acetylphenylglyoxilic Acid

o-Acetylphenylglyoxilic acid is a white substance that crystallizes from water as a monohydrate with a m.p. of 72°. The acid is freely soluble in alcohol, ether, and benzene; it is soluble in an aqueous solution of soda. Heating it with silver ammoniate yields metallic silver. Lead acetate precipitates a lead salt from an aqueous alcoholic solution. For analysis the o-acetylphenylglyoxilic acid monohydrate was recrystallized once from benzene and twice from water and dried in the air.

Found %: C 57.11; H 4.86; M 207 (titration). $C_{10}H_8O_4 \cdot H_2O$. Computed %: C 57.14; H 4.76; M 210. Number of active hydrogen atoms, determined by the Terentyev method: 4.03 and 3.74.

a) Determination of the water of crystallization. A weighed sample of the acid in question was dried in a 5-mm vacuum at 80° to constant weight.

Found %: H_2O 8.61; $C_{10}H_8O_4 \cdot H_2O$. Computed %: H_2O 8.57.

The melting point of the anhydrous substance was 123-124°. Recrystallization from water reconverted it into the original monohydrate with a m.p. of 72°.

Number of active hydrogen groups in the anhydrous substance, determined by the Terentyev method: 2.36 and 2.18.

b) Silver salt. 1.0 g of o-acetylphenylglyoxilic acid was mixed with 6 ml of water and then accurately neutralized with a 5% solution of ammonia. 1-2 drops of a 5% solution of silver nitrate was added to the resulting solution, and the flocculent grayish precipitate was quickly filtered out. A solution of 0.7 g of silver nitrate in 2 ml of water was added to the highly chilled filtrate. The white precipitate was filtered out, washed with a small quantity of cold water, then with alcohol, and lastly with ether. The salt was dried in a 5-mm vacuum at 20° to constant weight. This yielded 1.2 g (84%) of the silver salt.

Found %: C 40.32; H 2.61. $C_{10}H_7O_4Ag$. Computed %: C 40.13; H 2.34.

c) Methyl ester. 1.0 g of the silver salt was placed in 10 ml of methyl iodide. The salt dissolved instantaneously, and 10 to 15 seconds later a yellow precipitate of silver iodide settled out. The precipitate was filtered 30 minutes later and washed with ether. The resulting solution was evaporated to dryness. The residue consisted of 0.5 g (72%) of the methyl ester of o-acetylphenylglyoxilic acid, as a light-yellow, oily substance that rapidly crystallized. It was recrystallized three times from di-isoamyl ether and carefully washed with hexane. M.p. 92°.

Found %: C 64.15; H 4.91. $C_{11}H_{10}O_4$. Computed %: C 64.07; H 4.85.
Number of active hydrogen atoms, determined by the Terentyev method: 0.97 and 1.19.

Saponification of the methyl ester. 1 g of the substance was boiled for 10 minutes with 10 ml of 10% sulfuric acid. Extraction of the resulting solution with ether yielded 0.9 g of an oily substance, which rapidly changed into the crystalline monohydrate of o-acetylphenylglyoxilic acid, with a m.p. of 72° (from water).

d) Semicarbazone. 1.0 g of o-acetylphenylglyoxilic acid was dissolved in 10 ml of alcohol; 0.6 g of semicarbazide hydrochloride and 0.7 g of crystalline sodium acetate dissolved in 3 ml of water were added to the resulting solution. The next day the precipitate that settled was filtered out (weight 1.0 g). Recrystallization from water and drying in air yielded the semicarbazone monohydrate, which fused with decomposition at 158-160°.

Found %: C 49.24; H 4.93; H_2O 6.69. $C_{11}H_{11}O_4N_3 \cdot H_2O$. Computed %: C 49.44; H 4.87; H_2O 6.74.

e) Determination of the $-COCH_3$ group. In the usual Lieben reaction o-acetylphenylglyoxilic acid forms only extremely minute quantities of iodoform. It is therefore advisible to carry out the reaction under somewhat modified conditions. 0.20 g of o-acetylphenylglyoxilic acid was dissolved in 5 ml of water, and 1.85 g of iodine dissolved in 10 ml of a 20% aqueous solution of potassium iodide was added. Then 70 ml of a 10% aqueous solution of soda was added in the course of 45 minutes, and the reaction solution was allowed to stand at room temperature for 15 minutes. The color of the solution gradually turned light-yellow. The iodoform produced was extracted four times with ether. The resulting ether solution was washed with a dilute solution of sodium bisulfite and then desiccated with sodium sulfate. Driving off the ether yielded 0.12 g (32%) of iodoform with a m.p. of 119°.

f) Oxidation of o-acetylphenylglyoxilic acid with chromic anhydride. 1 g of the substance was dissolved in 25 ml of 10% sulfuric acid. A solution of 0.7 g of chromic anhydride in 10 ml of 10% sulfuric acid, chilled to -4° was added to the resultant solution, chilled to the same temperature. The reaction mixture was allowed to stand for 4-5 hours, the temperature slowly being raised from -4° to 18-20°. The solution gradually darkened, finally turning dark-brown. Two hours after reaction began a crystalline precipitate of indandione-1,3 was thrown down, the quantity precipitated gradually increasing. The precipitate was filtered out and washed with water. This yielded 0.2 g of an absolutely pure substance with m.p. of 131°, which exhibited no depression of the melting point when mixed with specially synthesized indandione-1,3 [8]. The compound recovered was also identified as 2-benzylidene-indandione 1,3 (m.p. 150-151°) and as the so-called bindone (m.p. 208°), which proved to be the same as a specially synthesized preparation, [8]. After the indandione-1,3 had been filtered out, the reaction solution was extracted five times with ether. The ether solution was desiccated with sodium sulfate and boiled with activated charcoal, after which the solvent was driven off. This yielded 0.2 g of a light-yellow, crystalline mass, slightly contaminated with an oily substance, which proved to be a mixture of phthalic acid and indandione-1,3. The mixture was separated by boiling it with ligroin. The white crystalline substance (0.1 g) that was insoluble in ligroin was phthalic acid with a temperature of decomposition of 198-200° (from water). Chilling the ligroin solution yielded 0.05 g of indandione-1,3 with m.p. of 131°. The aggregate yield of indandione-1,3 totaled 0.25 g (36%). After the acid reaction solution had been extracted with ether, a solution of soda was added to it (until its pH was 1), and it was evaporated at 40° in vacuum to dryness. The dry residue was extracted with ether in a Soxhlet apparatus for 10 hours. The ether solution was desiccated with sodium sulfate and boiled with animal charcoal, and the solvent was driven off. This left a mixture of phthalic and phthalonic acids, totaling 0.28 g, which was separated by treating it with a small quantity of ether in the cold; the phthalonic acid dissolved and thus could be separated from the phthalic acid. 0.15 g of the latter was recovered; it fused with decomposition at 200° (from water). The aggregate yield of phthalic acid totaled 0.25 g (31%). The solvent was driven off from the ether solution that contained the phthalonic acid; the oily residue was dissolved in a small amount of water, and the phthalonic acid was determined as its quinoxaline derivative by the method described in Report XI [14]. This yielded 0.004 g of the quinoxaline derivative. The yield of phthalonic acid totaled 3%.

3. Oxidative-Hydrolytic Transformation of 1,4-Naphthoquinone by Boiling It with a 1% Solution of Caustic Soda

20 g of 1,4-naphthoquinone was placed in 8 liters of a boiling 1% aqueous solution of caustic soda. The naphthoquinone dissolved gradually, the solution darkening and turning completely black as boiling was continued for a total of 8 hours. A strong current of air was passed through the solution uninterruptedly throughout the reaction. When the heating was over, the solution pH was adjusted to7.5-8 by adding 10% sulfuric acid. Then the reaction mass was reduced to a volume of some 2 liters and strongly acidulated with 80% sulfuric acid. The precipitated tarry mass was filtered out, and a solution of caustic soda was added to the light-yellow solution until its reaction with Congo red was slightly acid, after which the solution was evaporated at 50° in vacuum to dryness. The residue was extracted with ether in a Soxhlet apparatus for 16 hours, and the resulting ether solution was evaporated to 10 ml. The crystalline precipitate was filtered out and washed with a small amount of ether. This yielded 3.25 g of phthalic acid with a decomp. temp. of 198-200° (from water). All the ether was driven out of the ether filtrate, yielding an appreciable quantity of phthalic acid in addition, which weighed 1.1 g (after it had been placed on porous clay

and freed from the oily substance accompanying it). A total of 4.36 g (20%) of phthalic acid was recovered. The porous clay impregnated with the oily substance was boiled with ether, yielding 1.2 g of a yellow oil after the solvent had been driven off. The oil was boiled with 10 ml of hot water, cooled, and separated from the insoluble portion. The phthalonic acid was determined in the resulting aqueous solution as its quinoxaline derivative by the method described in Report XI [14]. This yielded 0.31 g of the quinoxaline derivative. The yield of phthalonic acid totaled 0.9%.

SUMMARY

It has been found that 3-hydroxy-1,4-naphthoquinone can be readily cleaved to acetylphenylglyoxilic acid by boiling it in aqueous buffer solutions with a pH ranging from 7.3 to 9.2.

It has been shown that the conditions and the nature of the hydrolytic cleavage of 3-hydroxy-1,4-naphthoquinone and of the previously investigated 2-methyl-3-hydroxy-1,4-naphthoquinone are practically identical.

LITERATURE CITED

[1] L. A.Shchukina, A.P.Kondratyeva, M.M.Shemyakin, J.Gen.Chem. 18, 1945 (1948).

[2] Ibid., J.Gen.Chem. 18, 2121 (1948).

[3] Ibid, J.Gen.Chem. 19, 183 (1949).*

[4] L.A.Shchukina and M.M.Shemyakin, J.Gen.Chem. 19, 193 (1949).**

[5] Yu.O.Shvetsov, L.A.Shchukina, and M.M.Shemyakin, J.Gen.Chem. 19, 498 (1949).***

[6] L.A.Shchukina, A.P.Kondratyeva, and M.M.Shemyakin, J.Gen.Chem. 19, 468 (1949).****

[7] A.P.Terentyev, K.D.Shcherbakova, J.Gen.Chem. 10, 2041 (1940); 15, 86 (1945); 16, 855 (1946).

[8] W.O.Teeters, R.L.Shriner, J.Am.Chem.Soc., 55, 3026 (1933).

[9] W.Wislicenus, A.Kötzle, Ann., 252, 72 (1889).

[10] M.M.Shemyakin and L.A.Shchukina, J.Gen.Chem. 18, 1925 (1948).

[11] A.I.Vinogradova, Yu.B.Shvetsov, and M.M.Shemyakin, J.Gen.Chem. 19, 507 (1949).*****

[12] D.P.Vitkovsky and M.M.Shemyakin, J.Gen.Chem. 21, 547 (1951).******

[13] Organic Syntheses, 21, 51, 91 (1941).

[14] L.A.Shchukina, Yu.B.Shvetsov, and M.M.Shemyakin, J.Gen.Chem. 21, 346 (1951).*******

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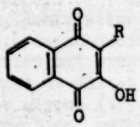
*See CB translations: *p. 165 ff; **p. 175 ff; ***447 ff; ****p. 419 ff; *****p. 457 ff; ******p. 607 ff; *******p. 381 ff.

OXIDATIVE AND OXIDATIVE-HYDROLYTIC TRANSFORMATIONS OF ORGANIC MOLECULES

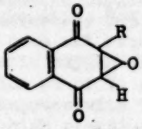
XV. THE TRANSFORMATIONS OF 1,4-NAPHTHOQUINONE OXIDE

L. A. Shchukina, A. S. Khokhlov and M. M. Shemyakin

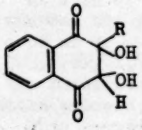
In our preceding reports it has been shown [1,2] that the conditions governing the hydrolytic cleavage of 3-hydroxy-1,4-naphthoquinone (I) and of 2-methyl-3-hydroxy-1,4-naphthoquinone (II), as well as the nature of this cleavage, were practically identical, which led us to conclude that substituting a methyl group for the hydrogen atom in the 2 position did not essentially affect the cleavage of these cyclic groups. In the course of these investigations it became necessary to determine whether such a change in molecular structure affected the properties or the transformations of the oxides and glycols of 1,4-naphthoquinone and of 2-methyl-1,4-naphthoquinone, the structure of which resembled that of the hydroxynaphthoquinones (I) and (II) studied earlier.



R = H (I)
R = CH_3 (II)



R = H (III)
R = CH_3 (IV)



R = H (V)
R = CH_3 (VI)

The oxide (IV) and the glycol (VI) have already been studied by us in detail [3,4]. As for the oxide (III) and the glycol (V), some of their properties have been described in two papers by T. Zincke [5,6], in which, however, several questions that interest us remain unanswered, so that we had to undertake a more detailed investigation of these two compounds. The simplest way of preparing the oxide is to react 1,4-naphthoquinone with hydrogen peroxide, while the glycol is formed from the former by boiling it with water [5,6].*

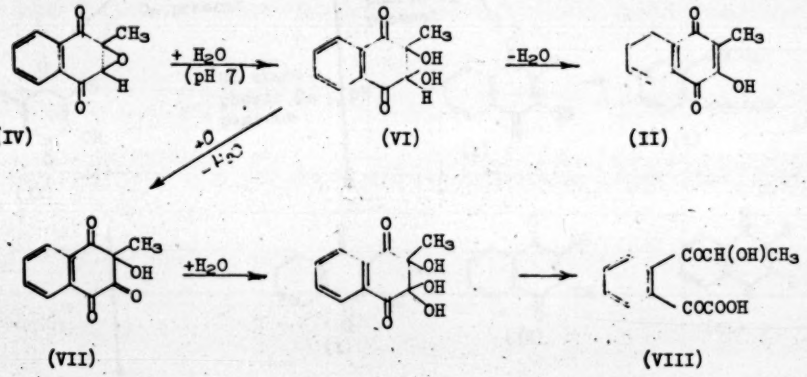
In line with the general trend of our researches, we were chiefly interested in comparing the behavior of the oxides and glycols of 1,4-naphthoquinone and 2-methyl-1,4-naphthoquinone under the conditions previously employed for the hydrolytic or oxidative-hydrolytic cleavage of carbocyclic compounds. We therefor ran a series of tests in which aqueous solutions of 1,4-naphthoquinone oxide, with different pH values, were boiled for certain periods of time with atmospheric oxygen present and excluded. It was found that in no case did the reaction

*The glycols (V) and (VI) are quite unstable compounds that readily suffer further changes when they are formed from the respective oxides by boiling the latter with water; we were therefore unable to isolate these glycols from the reaction solution in the pure state. Their presence in the solution was proved convincingly enough by an indirect method in the papers published previously [4-6].

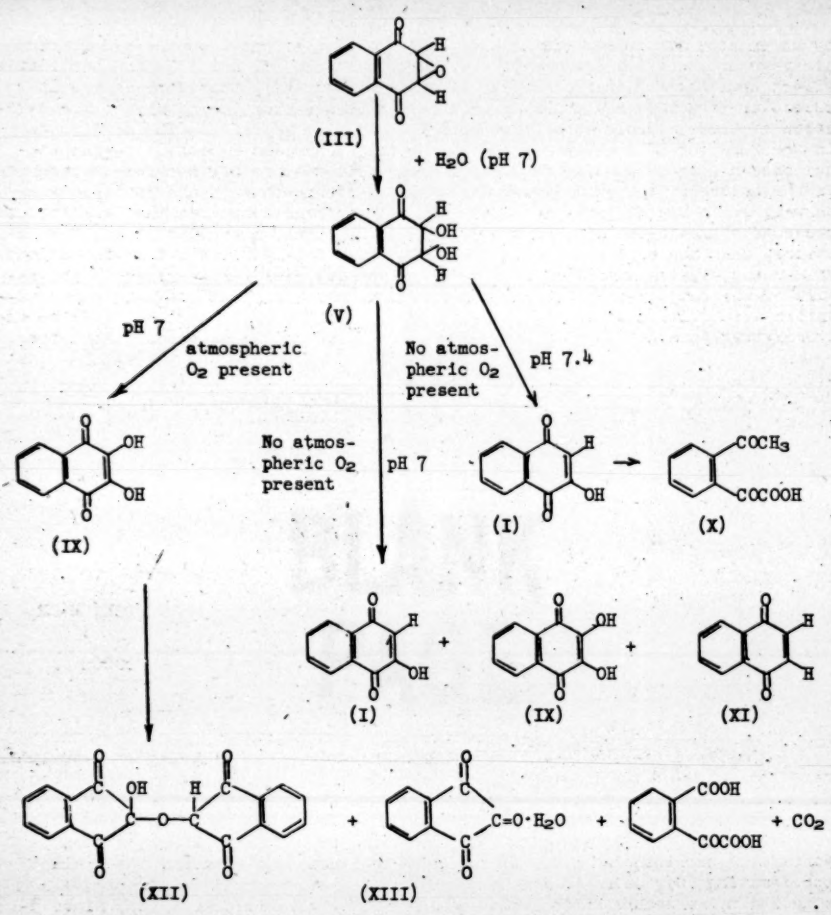
products contain any substances that might be considered to be compounds formed as the result of a purely hydrolytic cleavage of the cyclic grouping of 1,4-naphthoquinone oxide (III). The behavior of 2-methyl-1,4-naphthoquinone oxide (IV) is quite similar, its cyclic groupings not being cleaved hydrolytically under analogous conditions [3,4]. Still, neither oxide remained entirely unchanged when its aqueous solutions were heated (vide infra, as well as [3-6]), inasmuch as both of them are readily hydrated, being converted into the respective glycols (V) and (VI), which then undergo a series of subsequent changes, occurring for the most part along two competing lines. One of these lines is the dehydration of the glycols to the respective hydroxynaphthoquinones (I) and (II), while the other involves the oxidation of the glycols, either by atmospheric oxygen or by the as yet unchanged original oxide. The difference in the structure of the intermediate glycols does not exert a very marked effect upon the readiness with which they can be dehydrated. In fact, the emergency of the hydroxynaphthoquinones is observed when aqueous solutions of the oxides of 1,4-naphthoquinone or of 2-methyl-1,4-naphthoquinone are boiled. It should likewise be noted that 2-methyl-1,4-naphthoquinone oxide (IV) is more prone to change into the corresponding hydroxynaphthoquinone than the 1,4-naphthoquinone oxide (III). When an aqueous solution of the oxide (IV) (initial pH 7) is boiled for 24 hours with no atmospheric oxygen present, the yield of the 2-methyl-3-hydroxy-1,4-naphthoquinone is 75% [3], whereas the yield of 3-hydroxy-1,4-naphthoquinone (I) from the oxide (III) is only 30% under the same conditions (cf the experimental section). The external reaction conditions, especially the pH of the medium and the presence or absence of oxidizing agents, exert an incomparably greater effect upon the dehydration of the glycols (V) and (VI). Our data indicate that the dehydration of the glycol (V), formed from the oxide (III), becomes the dominating reaction whenever the process is carried out in a boiling buffer solution at a pH in excess of 7 with atmospheric oxygen excluded. At a pH of 7.4, for instance, dehydration is approximately 80% complete, whereas the yield of 3-hydroxy-1,4-naphthoquinone (I) does not exceed 30% at a pH of 7. When the reaction is carried out with atmospheric oxygen present, no 3-hydroxy-1,4-naphthoquinone is formed at all at a solution pH of 7, since then the oxidation of the intermediate glycol (V), which competes with the dehydration process, becomes the sole reaction, owing to its high reaction velocity. This second line taken by the process is observed when aqueous solutions of the oxides are boiled, this applying to the 1,4-naphthoquinone oxide as well as to the 2-methyl-1,4-naphthoquinone oxide (cf [3,4] and vide infra). It predominates most, to be sure, when oxidizing agents (such as atmospheric oxygen) are present and at a solution pH of 7, since the dehydration of the intermediate glycols is rather slow at that pH. Oxidative transformations may take place even when no atmospheric oxygen is present (provided the solution pH does not exceed 7), the role of an oxidizing agent then being taken over, evidently, by the initial oxides, which are reduced to the respective quinones, small quantities of the latter being recoverable after the conclusion of the reaction.

It should be stressed at this point that the rate at which the intermediate glycols are oxidized, as well as the nature of the resulting oxidation products, largely depend upon the structure of the initial oxides. In this respect, there is a considerable difference between this course followed by the process and the dehydration reaction, which is similar for the glycols of 1,4-naphthoquinone and 2-methyl-1,4-naphthoquinone. In the 2-methyl-1,4-naphthoquinone oxide (IV), for example, oxidation of the intermediate glycol (VI) results in formation of a hydroxy-triketone (VII) [3,4], whereas our data indicate that the initial product of the oxidation of the glycol (V), secured from 1,4-naphthoquinone oxide (III), is isonaphthazarine (IX) (cf the subjoined diagram). The velocities of these processes also differ sharply – in the second case the oxidation reaction is much faster than in the first. Hence, although substituting a methyl group for the

hydrogen atom in the 2 position has practically no effect upon the hydrolytic cleavage of the cyclic groups of the hydroxyquinones (I) and (II) and but little effect upon the dehydration of the glycols (V) and (VI), this same change in molecular structure has a very pronounced influence upon the nature of the oxidation of these glycols as well as upon the reaction velocity. The difference in the behavior of the glycols of 1,4-naphthoquinone and 2-methyl-1,4-naphthoquinone when acted upon by an oxidizing agent is responsible for the differences in the nature of the oxidative-hydrolytic transformations of the initial oxides, as well as in the differences in the structure of the compounds that are the end products of reactions of this nature. It has been shown earlier [3,4], for instance, that the principal products of the oxidative-hydrolytic transformations of 2-methyl-1,4-naphthoquinone oxide (IV) are phthiocol (II) [formed as the result of the dehydration of the intermediate glycol (VII)] and o-lactylphenylglyoxilic acid (VIII), produced by the initial oxidation of this glycol (VI) to the hydroxytriketone (VII) and the ensuing hydrolytic transformation of the latter:



A totally different result is secured, however, in the oxidative-hydrolytic transformations of the 1,4-naphthoquinone oxide (III); here the nature of the end products is largely governed by the conditions under which the process is carried out. We have found, in fact, that carrying out the reaction at a pH of 7.4 in a boiling buffer solution, with atmospheric oxygen excluded, yields 3-hydroxy-1,4-naphthoquinone (I) as the principal reaction product, its yield approximating 70%, owing to the dehydration of the intermediate glycol (V). In addition, we secure up to 10% of o-acetylphenylglyoxilic acid (X), since 3-hydroxy-1,4-naphthoquinone is partially cleaved hydrolytically under these conditions (cf [2]). Provided the initial pH of the solution is 7 and the other experimental conditions remain the same, the yield of the 3-hydroxy-1,4-naphthoquinone (I) will not exceed 30%, while there will be no o-acetylphenylglyoxilic acid (X) at all among the reaction products, inasmuch as lowering the pH of the solution to 7 greatly interferes with the dehydration of the glycol (V) and the hydrolytic cleavage of the hydroxynaphthoquinone (I), as has been shown earlier. At the same time, up to 50% of isonaphthazarine (IX) may be recovered, formed evidently as the result of the oxidation of the intermediate glycol (V) by the original oxide (III) and by the 1,4-naphthoquinone (XI) formed from the glycol (cf [4]). The results secured are wholly different when the reaction solution is boiled with atmospheric oxygen present. When the initial pH of the solution is 7, the intermediate glycol (V) is merely oxidized to isonaphthazarine (IX), the yield of which is 85% after six hours of boiling. No 3-hydroxy-1,4-naphthoquinone (I) is formed under these conditinns. The resulting isonaphthazarine



(IX) gradually begins to undergo further changes, however, ending up as ninhydrin (XIII) and phthalonic acid. After 30 hours of boiling, the yield of the first of these two compounds exceeds 20%, and that of the latter 30%. At the same time hydrindanthin (XII) is formed, a substance with the empirical formula $C_{20}H_{12}O_8$, together with a large amount of carbon dioxide.*

Comparison of the results of the researches set forth above with those described previously [3,4] indicates that whereas substituting a methyl group for the hydrogen atom in the 2-position in the 3-hydroxy-1,4-naphthoquinone (I) molecule does not affect the conditions or the nature of the hydrolytic cleavage

*See our next report for the conversion of isonaphthazarine into ninhydrin, hydrindanthin and phthalonic acid.

of the cyclic grouping, a similar substitution in the molecule of the corresponding oxide (III) results in a marked change in the course of the oxidative-hydrolytic transformations. The reason for this is the circumstance that the glycols (V) and (VI) formed as the result of the hydration of the original oxides (III) and (IV) are oxidized differently.

EXPERIMENTAL *

1. Oxidative-hydrolytic transformations of 1,4-naphthoquinone when no atmospheric oxygen is present.

a) By boiling in water. This experiment was carried out in the apparatus described in our preceding report [2], in Experiment 1,e. Three liters of water was poured into the reaction flask, 6 g of 1,4-naphthoquinone oxide being placed in the glass container located above the level of the water. ** The water was boiled and the air driven out by an inert gas for four hours, after which the container with the quinone was immersed in the water, and boiling was continued for another 24 hours. The solution quickly turned brownish-red, the color persisting to the end of boiling. The reaction mass was then evaporated to dryness in vacuum, in an atmosphere of the inert gas. The yellow aqueous distillate was acidulated with 20 ml of 50% sulfuric acid and extracted 3 times with ether. The ether solution was desiccated with sodium sulfate, and the ether was driven off, yielding 0.15 g of 3-hydroxy-1,4-naphthoquinone, with a m.p. of 188-189°. The dry residue left after the reaction mass had been evaporated was boiled for one hour with 750 ml of ether, cooled, and filtered out. The ether-insoluble red crystalline substance (weighing 2.8 g) fused at 280° and exhibited no depression of the melting point when mixed with isonaphthazarine.*** The ether solution was extracted four times with a 5% soda solution and then two times with water, the latter being added to the soda extracts. The ether solution was desiccated with sodium sulfate, and the ether was driven off. This left 0.22 g of a dark substance, which was sublimed in vacuum. This yielded yellow crystals that fused at 126-127° and exhibited no depression of the melting point when mixed with 1,4-naphthoquinone. The soda solution was acidulated with 10% sulfuric acid until its reaction with Congo red was acid and then extracted repeatedly with ether. The ether solution was desiccated with sodium sulfate, and the ether was driven off. The residue was a mixture of isonaphthazarine and 3-hydroxy-1,4-naphthoquinone, contaminated with highly tarred substances. We developed a special method for separating these two quinones, based upon the markedly different solubilities of their lead salts in water. The lead salt of isonaphthazarine is practically insoluble even in hot water, whereas the lead salt of 3-hydroxy-1,4-naphthoquinone settles out only after standing for a long time. We therefore dissolved the resultant mixture of quinones in 500 ml of boiling water and added 20 ml of a 10% solution of lead acetate to the hot solution. The lead salt of isonaphthazarine that settled as a blue precipitate was filtered out. When this salt was decomposed with 50 ml of 5% nitric acid, we secured 0.5 g of isonaphthazarine, with a b.p. of 281° (from alcohol). The total isonaphthazarine recovered was 3.3 g (50%). After the lead salt of isonaphthazarine had been filtered out, the filtrate was acidulated with 50 ml of 20% sulfuric acid and extracted several times with ether. The ether solution was

* The analytical part of this research was performed with the assistance of E. A. Ignatyeva, and we wish to express our profound indebtedness to her.

** The 1,4-naphthoquinone oxide was prepared by reacting an alcoholic solution of 1,4-naphthoquinone with hydrogen peroxide and an aqueous solution of soda [7]. The Melting point of 1,4-naphthoquinone oxide is 134-135° (from alcohol).

*** The isonaphthazarine was prepared by oxidizing 1,2-naphthoquinone with a solution of bleaching powder [8]. M.P. 282° (from acetic acid).

desiccated with sodium sulfate, and the ether was driven off. This yielded 2.4 g of a yellow substance, which fused at 189-191° after recrystallization from methanol and exhibited no depression of the melting point when mixed with 3-hydroxy-1,4-naphthoquinone. It weighed 0.6 g. A total of 1.8 g (30%) of 3-hydroxy-1,4-naphthoquinone was recovered.

b) By boiling in a buffer solution (pH 7.4). This experiment was run in the apparatus described in our preceding report [2], in Experiment 1,e. 1.3 g of a phosphate buffer solution (pH 7.4; buffer capacity 2/15 mole) was poured into the reaction flask, while 2.5 g of 1,4-naphthoquinone oxide was placed in a glass container located above the level of the liquid. The buffer solution was boiled for four hours while the oxygen was driven out of the system by an inert gas, after which the container with the quinone was lowered into the solution and boiling was continued for 48 hours. Then the reaction mass was cooled in an atmosphere of the inert gas, acidulated with a previously determined quantity of sulfuric acid until its pH was about 4.0, and evaporated in an atmosphere of the inert gas to a volume of 250 ml. The yellow crystalline precipitate that settled out as the solution cooled was filtered out and washed with a small amount of water. Weight 1.9 g (Precipitate No. 1). The pH was brought to 4.0 again, and the solution was evaporated to dryness in an atmosphere of the inert gas. The dry residue was extracted with ether in a Soxhlet apparatus. Driving off the ether yielded 0.4 g of an oily residue (Residue No. 2.).

Investigation of Precipitate No. 1. The precipitate was heated with 300 ml of ether, and 0.2 g of an insoluble, highly tarred, black substance was filtered out. The ether solution was extracted three times with a 10% solution of soda and washed twice with water, the water being added to the soda solution. The ether solution contained neither 1,4-naphthoquinone nor any other neutral substances. The soda solution was acidulated with 20% sulfuric acid until its reaction was acid with Congo red and then extracted three times with ether. The ether solution yielded 1.7 g (68%) of 3-hydroxy-1,4-naphthoquinone, with a m.p. of 189-191° (from methanol).

Investigation of Residue No. 2. The o-acetylphenylglyoxilic acid present in the oily residue was isolated as the respective semicarbazone by dissolving the residue in 3 ml of 20% alcohol and then adding 0.4 g of semicarbazide hydrochloride and 0.4 g of crystalline sodium acetate dissolved in 2 ml of water. Two days later the precipitated semicarbazone was filtered out. Weight: 0.3 g. It fused with decomposition at 158-160° after recrystallization from 50% alcohol and exhibited no depression of the decomposition temperature when mixed with the semicarbazone of o-acetylphenylglyoxilic acid, described in the previous report [2]. Yield: 8 %.

2. Oxidative-hydrolytic cleavage of 1,4-naphthoquinone oxide in the presence of atmospheric oxygen.

a) By boiling in water for 30 hours. Three liters of water and 6 g of 1,4-naphthoquinone were placed in a flask fitted with a reflux condenser and a tube extending to the bottom of the flask, through which a powerful current of air was passed throughout the experiment. The reaction mixture was boiled for 30 hours. Upon cooling, the dark, tarry precipitate was filtered out. Weight: 0.35 g. The mother liquor was evaporated at 60° and 10 mm to a volume of 150 ml, and the red precipitate that settled was filtered out. Weight: 1.3 g (Precipitate No. 1). 10 ml of a 10% aqueous solution of lead acetate was added to the filtrate and the precipitated blue lead salt (weight: 0.35 g) was filtered out. This lead salt was treated with 5 ml of a 5% solution of nitric acid, and the precipitate was filtered out, yielding 0.15 g of a red crystalline substance with a m.p. of 281°, which fused at the same temperature when mixed with a specially synthesized preparation of isonaphthazarine. After the lead salt of isonaphthazarine had been

filtered out, about 100 ml of a 10% aqueous solution of lead acetate was added to the reaction solution (until no more precipitate was thrown down), and the precipitated lead salt was filtered out. Weight: 3.9 g (Precipitate No. 2). The filtrate was acidulated with sulfuric acid until its reaction with Congo red was slightly acid and then evaporated in vacuum to dryness.* The dry residue was extracted with ether for 6 hours in a Soxhlet apparatus. Driving off the ether left behind 2.7 g of an orange-yellow oil (Residue No. 3).

Investigation of Precipitate No. 1. 1.3 g of the red substance was treated with 50 ml of a 5% soda solution. The undissolved light-yellow precipitate was filtered out and washed with water. Weight: 0.35 g (6%). Double recrystallization from a small quantity of alcohol yielded 0.25 g of a substance that fused at 247-249° (with decomposition).

Found %: C 68.85; H 3.28. $C_{20}H_{12}O_8$. Computed %: C 68.96; H 3.45.
The molecular weight was determined cryoscopically in nitrobenzene.
Found: M 346, 354. $C_{20}H_{12}O_8$. Computed: M 348.

The soda solution secured above was acidulated with 20% sulfuric acid, and the resultant precipitate was filtered out. This yielded 0.95 g of a substance with a m.p. of 281°, which fused at the same temperature when mixed with isonaphthazarine. The aggregate yield of isonaphthazarine totaled 1.1 g (17%).

Investigation of Precipitate No. 2. This precipitate, which was a mixture of the lead salts of hydrindanthine, ninhydrin, and phthalonic acid, was divided into two parts. The hydrindanthine was determined in one part, while the ninhydrin and the phthalonic acid were determined in the other. 1.5 g of the mixture of lead salts was dissolved in 10 ml of a 5% solution of nitric acid, and the precipitated hydrindanthine was filtered out. Weight: 0.1 g; yield: 4%. Recrystallization from a 1:3 acetone-chloroform mixture and drying to constant weight in a 10-mm vacuum at 90° yielded a substance with a m.p. of 229°, which exhibited no depression of the melting point when mixed with the hydrindanthine prepared by reducing ninhydrin with stannous chloride [8].

Found %: C 66.86; H 3.46. $C_{18}H_{10}O_8$. Computed %: C 67.08; H 3.11.

The rest of the precipitated lead salts was treated with 50 ml of 10% sulfuric acid; the precipitated lead sulfate was filtered out and washed with water. The mother liquors were extracted four times with ether, the ether solution was desiccated with sodium sulfate, and the ether was driven off. The residue was 1.7 g of an oily substance (Residue No. 4.) The latter, like the previously isolated Residue No. 3, was a mixture of hydrindanthine, ninhydrin, and phthalonic acid. The two residues were therefore combined and dissolved in 100 ml of water, and 5 g of o-phenylenediamine dissolved in 150 ml of water was added to the resultant solution. A yellow precipitate of ketohydrindenophenazine was thrown down at once; it was filtered out 3 to 4 minutes later and washed with water (Precipitate No. 5). Weight: 1.4 g. In view of the amount of ninhydrin contained in the 1.5 g of the lead salts previously taken to isolate the hydrindanthine, the yield of ninhydrin was 22%. An appreciable precipitate settled out of the mother liquor after the latter had been standing for a day; it was filtered out. Weight: 3.5 g (Precipitate No. 6).

Investigation of Precipitate No. 5. The obtained ketohydrindenophenazine is formed as a result of the interaction of o-phenylenediamine both with ninhydrin and with hydrindantin. After recrystallization from alcohol the compound has m.p. 220-220.5° and does not give a depression of the melting point in admixture with

*To facilitate the extraction of the residue left after evaporation from the flask, 80 ml of sodium sulfate was added to the solution before it was evaporated.

ketohydrindenophenazine prepared by reaction of ninhydrin with o-phenylenediamine.

Found %: C 77.86; H 3.53: $C_{15}H_8ON_2$. Computed %: C 77.59; H 3.45.

Investigation of Precipitate No. 6. This precipitate, which was contaminated with a small quantity of tar, was triturated with 10 ml of acetone. The undissolved substance was filtered out and washed with two 5-ml batches of acetone. Weight 3.4 g. Double recrystallization from alcohol containing activated charcoal yielded a white crystalline substance with a temp. decomp. of 209-210°, which was the previously described o-phenylenediamine salt of the quinoxaline derivative of phthalonic acid [11]. The yield was 33% (allowing for the phthalonic acid present in the 1.5 g of lead salts used for the recovery of the hydrindanthine).

Found %: C 67.22; H 4.66; N 14.77. $C_{21}H_{18}O_3N_4$. Computed %: C 67.35; H 4.81; N 14.94.

The chemical nature of the synthesized salt was finally established by decomposing it to the corresponding free acid. 0.5 g of the salt was dissolved in 25 ml of 10% NaOH, and the solution was extracted with ether. 0.1 g of o-phenylenediamine, with a m.p. of 101°, was recovered from the ether solution. The alkaline solution was acidulated with 10% sulfuric acid; this caused 0.3 g of the quinoxaline derivative of phthalonic acid, with a m.p. of 240° (from alcohol) to settle out. The substance recovered was identical with the preparation described previously [11].

b) By boiling in water for 6 hours. 1.5 liters of water and 3 g of 1,4-naphthoquinone oxide were placed in a flask fitted with a reflux condenser and a tube extending down to the bottom of the flask, through which a strong current of air was passed throughout the experiment. The mixture was boiled for 6 hours, after which the solution was cooled and the red precipitate of isonaphthazarine was filtered out. Weight: 2.1 g. M.p. 282° (from acetic acid). The reaction solution was evaporated at 60° in vacuum to a volume of 100 ml, and another 0.7 g of isonaphthazarine was filtered out. The total yield of isonaphthazarine was 2.8 g (85%). Fourfold extraction of the aqueous solution with ether and processing of the ether extracts yielded 0.2 g of an oily substance, which was dissolved in 10 ml of water. The resultant precipitate of ketohydrindenophenazine was filtered out. Weight: 0.15 g; m.p. 220° (from alcohol) [10]. The mother liquor was set aside to stand overnight, and the next day 3 ml of a 10% solution of caustic soda was added, followed by 10 ml of a 20% solution of sulfuric acid, after which the whole was extracted five times with ether. After the ether solution had been desiccated and the ether had been driven off, we secured 0.1 g of the quinoxaline derivative of phthalonic acid, with a m.p. of 239° (from alcohol)[11].

SUMMARY

A study has been made of the transformation of 1,4-naphthoquinone oxide produced by boiling its aqueous solutions under various conditions. It has been shown that the glycol formed as the initial reaction product from the original oxide is dehydrated, on the one hand, to 3-hydroxy-1,4-naphthoquinone and, on the other, is oxidized to isonaphthazarine, the trend of these reactions largely depending upon the pH of the solution and whether an oxidizing agent (atmospheric oxygen) is present. The 3-hydroxy-1,4-naphthoquinone and isonaphthazarine produced in these reactions can, in turn, undergo further oxidative-hydrolytic transformations. When the solution pH exceeds 7, the first of these compounds is cleaved to o-acetylphenylglyoxilic acid when no atmospheric oxygen is present.

As for the isonaphthazarine, it undergoes far-reaching changes when atmospheric oxygen is present, the reaction end products being ninhydrin, hydrindanthine, and phthalonic acid. The oxidative-hydrolytic transformations of the oxide and glycol of 1,4-naphthoquinone differ markedly from the analogous transformations of the oxide and glycol of 2-methyl-1,4-naphthoquinone investigated previously.

LITERATURE CITED

[1] L.A.Shchukina, A.P.Kondratyeva, and M.M.Shemyakin, J.Gen.Chem. 18, 2121 (1948).

[2] L.A.Shchukina, A.S.Khokhlov, and M.M.Shemyakin, J.Gen.Chem. 21, 908 (1951).*

[3] L.A.Shchukina, A.P.Kondratyeva, and M.M.Shemyakin, J.Gen.Chem. 19, 183 (1949).**

[4] L.A.Shchukina and M.M.Shemyakin, J.Gen.Chem. 19, 193 (1949).***

[5] Th. Zincke, Ber., 25, 3599 (1892).

[6] Th. Zincke, B.Wiegand, Ann., 286, 58 (1895).

[7] L.F.Fieser, W.P.Campbell, E.M.Fry, M.D.Gates, Jr., J.Am.Chem.Soc., 61, 3216 (1939).

[8] Th. Zincke, A. Ossenbeck, Ann., 307, 1 (1899).

[9] S.Ruhemann, J.Chem.Soc., 99, 792 (1911).

[10] S.Ruhemann, J.Chem.Soc. 97, 1438 (1910).

[11] L.A.Shchukina, A.P.Kondratyeva, and M.M.Shemyakin, J.Gen.Chem. 19, 468 (1949).****

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See CB translations: *p.997 ff; **p.165 ff; ***175 ff; ****419 ff.

THE MICROSTRUCTURE OF PROTEIN

VIII. THE ACTION OF OXALYLCHLORIDE UPON DIKETOPIPERAZINE AND THE ENSUING TRANSFORMATION OF THE PRODUCTS OF THIS REACTION INTO AMIDINE

N. I. Gavrilov and L. N. Akimova

In our preceding paper [1] we have deciphered to the last detail the mechanism by which acylated cyclic amides (diacetyl-diketopiperazine and dichloroacetyl-diketopiperazine) react with amino acids, which had been previously observed by Bergmann and explained by him as a simple reacylation of the latter by the acyl groups of the former.

Among the examples cited by Bergmann, however, there are instances that do not fit into our scheme. We still do not understand the acylating action of acyl-4-imidazole compounds (imidazole, histidine, histamine), in which it is hard to find a way for the formation of any intermediate amidine forms, having as their consequences the detaching of the acetyl group of the imidazole derivatives. We succeeded in discovering an explanation for this reaction in the amidine nature of imidazole itself. According to our experiments, the reaction with an acyl-5-imidazole derivative must be explained thus: an amine or an amino acid is added to the acyl group of the histidine as follows:

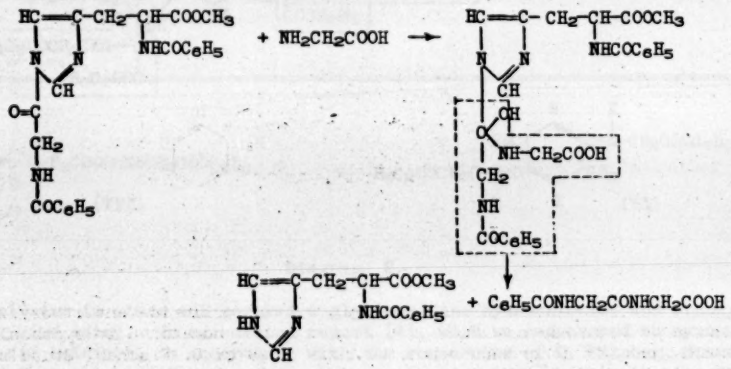


Diagram 1.

Like this reaction, which was discovered, though not explained, by Bergmann, we treated di-exo-ethoxyoxalyl-ethyl glycine – 2,5-dihydropyrazinamidine – with

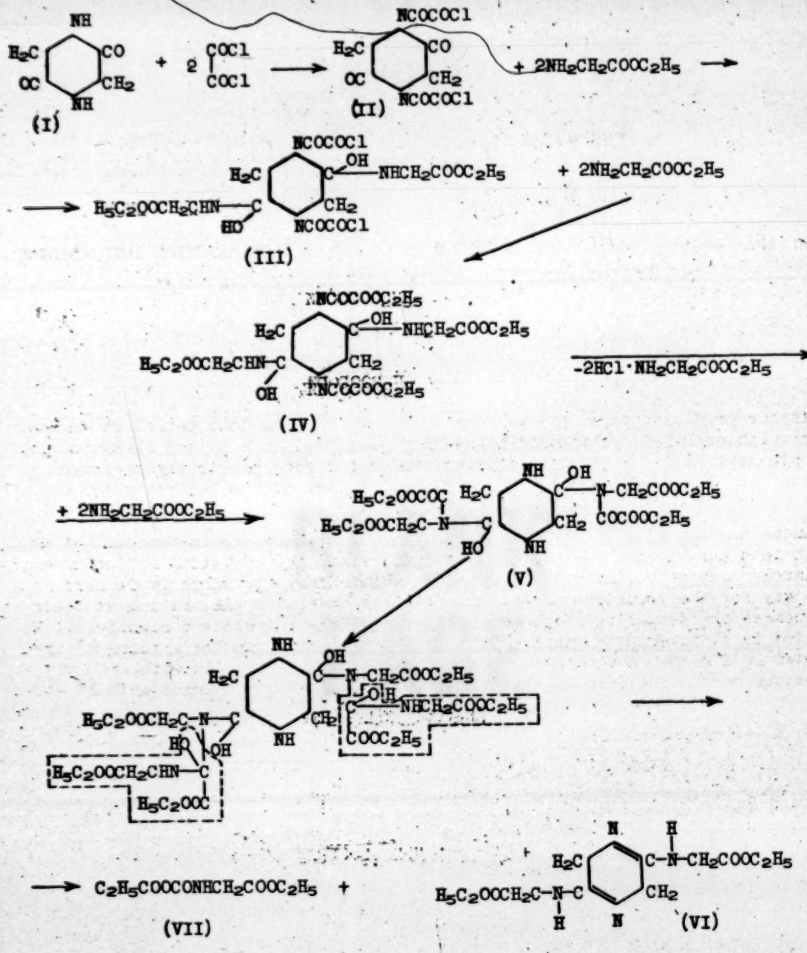


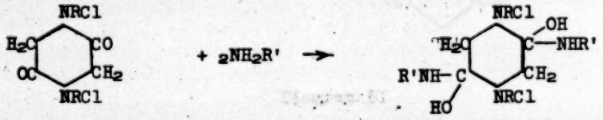
Diagram 2.

ethyl glycine in ether and secured a glycinamidine hydrochloride and ethoxyoxalyl-glycine ester. In our second report [3], when we endeavored to synthesize amino-acid amidines, in accordance with the researches of O. Fischer, Staudinger, and M.M.Shemyakin and Elkin, we chose to synthesize them by chlorinating diketopiperazine with oxalyl chloride. We isolated neither tetrachloropiperazine nor dichlorodihydropiperazine, as their formation was considered adequately demonstrated by the works of the authors cited [4,5,6], but eliminated the excess oxalyl chloride and effected a condensation with ethyl glycine.

In the light of the results we had secured, reported in our preceding paper [1], it became necessary to re-examine the synthesis of the amidine via the action of oxalyl chloride upon diketopiperazine. This made it necessary to provide a new diagram for the formation of the compounds whose formation had been described in Report 2 of this series [3].

We managed to demonstrate, by various examples, that a glycinamidine is not synthesized by the reaction of ethylglycine with dichlorodihydropiperazine or tetrachloropiperazine, but is the result of a reaction of this ester with diketopiperazine chloroxalated at a nitrogen atom. By way of confirming this we have isolated most of the intermediate compounds (Diagram 2).

Thus, the compounds we have isolated indicate that the formation of a glycinamidine must be regarded as taking place in several stages. The reactions of diketopiperazine with oxalyl chloride produces a quantitative yield of N,N'-dichloroxalyl-diketopiperazine (II). In this compound the chlorine atoms are not reactive, like the chlorine atoms in N,N'-dichloroacetyl-diketopiperazine. Reacting N,N'-dichloroxalyl-diketopiperazine with ethylglycine yields N,N'-exo-dichloroxalyldihydrate-2,5-ethyldiglycin-dihydropyrazinamidine (III), the formation of which follows the general lines of the reaction of an amino acid with a diketopiperazine derivative that is chloroxalated at a nitrogen atom (such as N,N'-dichloroacetyl-diketopiperazine).



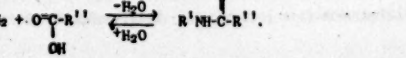
The use of an excess (4 moles) of ethylglycine evidently promotes its cyclization with the diketopiperazine. The resultant alcohol esterifies the chloroxalyl groups in the exo position, forming a di endo-N-ethoxyoxalylhydrate-2,5-dihydropyrazinamidine. Proof that the chloroxalyl groups are in that position, namely the endo position, is afforded by the fact that neither oxalyl-ethylglycine nor any traces of oxalyl-ethyldiglycine is found in the reaction products. The latter could be formed only if the chloroxalyl groups were in the exo position.

Cyclization of the excess ethylglycine is the only source for the formation of ethoxy groups, the more so as we always find the requisite amount of diketopiperazine needed for this among the reaction products.

What is still unclear is whether the ethoxy groups are formed before or after the rearrangement of the chloroacyl groups in the exo position. Nevertheless, the formation of an ethoxy derivative results in the recovery of the di-exo-N- diethoxyoxalyl-ethylglycine ester of 2,5-dihydropyrazinamidine dihydrate. We were most interested in the reaction of this diethoxyoxalyl derivative of the amidine with another batch of ethylglycine. This reaction parallels the transformations of acylated imidazole, 2 more moles of ethylglycine combine with the ethoxyoxalyl groups to form an ethoxyoxalylglycine ester, thus releasing the glycinamidine.

Thus, our previous diagram proved to be incorrect, the glycinamidine not being formed via the diketopiperazine chloride but resulting from an amidine condensation of acylated diketopiperazine.*

Note. Our study of n-acylated diketopiperazines and amidines leads us to conclude that the synthesis of a peptide bond does not take place directly, via the reversible reaction:



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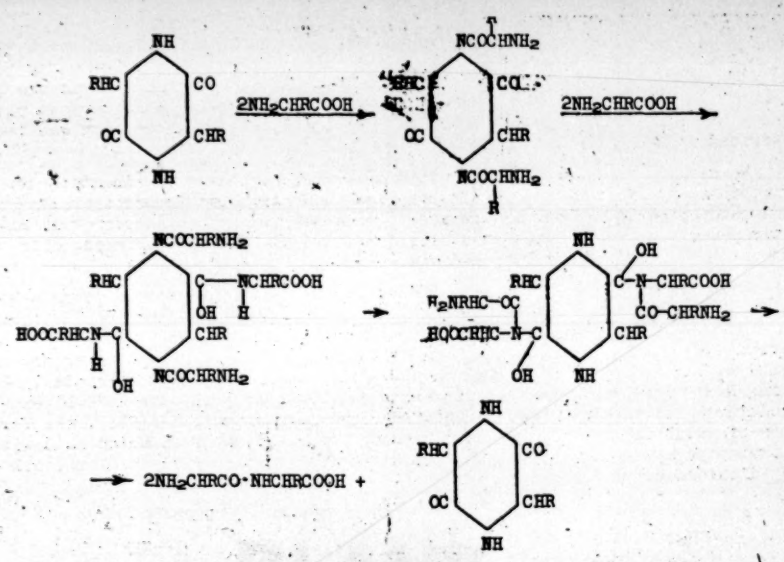

Diagram 3.

EXPERIMENTAL

Action of oxalyl chloride upon diketopiperazine. 20 ml of oxalyl chloride added to 3 g of diketopiperazine, pulverized in a mortar and placed in a Gavrilov apparatus [7], and the mixture was gently boiled over an electric lamp for 16 hours. The precipitate within the apparatus was filtered out and washed with absolute ether until the odor of oxalyl chloride had disappeared. The resultant light-yellow substance was dried in a vacuum desiccator. Weight: 7.3 g (94% of the theoretical). M.p. 184° (with decomposition). Properties: sparingly soluble in chloroform and acetone, more soluble in methyl acetate. It reacts with alcohols.

Found %: C 32.61; H 1.58; N 9.30, 0.23 (Kjeldahl); Cl 23.87 (Volhard). $C_8H_4O_6N_2Cl_2$. Computed %: C 32.54; H 1.36; N 9.49; Cl 24.01.

The substance synthesized was N,N'-dichloroxalyldiketopiperazine (II).

Determination of oxalic acid after hydrolysis (permanganatometry). Found: 69.10 mg; computed 69.75 mg.

Condensation of N,N'-dichloroxalyl-diketopiperazine with 2 moles of ethylglycine. 35 ml of absolute ether was added to 3 g of N,N'-dichloroxalyl-diketopiperazine, and 2.1 g of ethylglycine in ether was added to the mixture at room temperature, with mechanical stirring. After the reaction had gone on for 30 minutes, the precipitate was filtered out and washed with absolute ether. The

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but with the aid of acylated (acetylated, phosphorylated, aminoacylic, etc) diketopiperazines. (Diagram 3).

precipitate was re-treated with chloroform and filtered out.

The ether filtrate was allowed to stand overnight, a minute quantity of diketopiperazine settling out. The refiltered ether solution was then concentrated to dryness in vacuum. The residue was recrystallized from water and dried in a vacuum desiccator. M.p. 143°. The substance was readily soluble in chloroform and in benzene and proved to be ethyloxalyldiglycine, the melting point of which is 143° according to the literature [8]. We recovered a few milligrams. The oxalyldiglycine ester with a m.p. of 143° was likewise recovered from the chloroform solution.

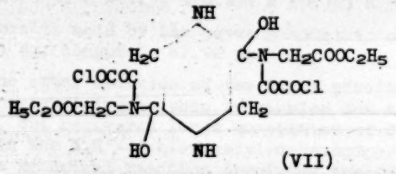
The precipitate that had been processed with ether and chloroform was extracted with anhydrous acetone in an extractor. The acetone extract was allowed to stand overnight, and the next morning the crystals that had settled were filtered out and washed with ether. They had a m.p. of 146-148° after having been dried in a vacuum desiccator. Properties: the substance is sparingly soluble in water, chloroform, benzene, and ether. When the precipitate was treated with methanol on a slide, diketopiperazine was observed to form under a microscope. The substance exhibited a positive reaction for chlorine and positive anhydride, ninhydrin, and biuret reactions. The last reaction was of the dipeptide type.

Found %: C 38.45; H 4.43; N 11.46 (Kjeldahl); Cl 14.51 (Volhard); M 493 (Rast). $C_{16}H_{23}O_{10}N_4Cl_2$. Computed %: C 38.32; H 4.39; N 11.18; Cl 15.17; M 501.

Determination of oxalic acid by the permanganometric method (after hydrolysis). Found: 19.09 mg, computed 19.51 mg.

The recovery of minute quantities of ethyloxalyldiglycine and diketopiperazine is evidence of the general nature of the acyl group shift – in the present case the chloroxalyl shifting from the endo to the exo position.

The foregoing data indicate that the substance synthesized is the N,N'-exo-dichloroxalyldihydrate-2,5-ethyldiglycine-dihydropyrazinamidine (VII).



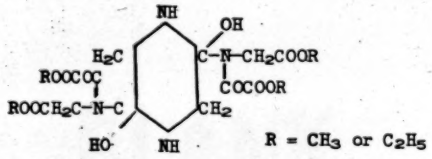
(VII)

Condensation of N,N'-dichloroxalyl-diketopiperazine with 4 moles of ethylglycine. 6 g of N,N'-dichloroxalyl-diketopiperazine was mixed with 50 ml of absolute ether, and 8.4 g of ethylglycine was added to the chilled mixture, which was stirred mechanically. The ethylglycine was added in the course of half an hour. The medium was acid. The precipitate was filtered out and washed with absolute ether.

The precipitate was processed in the cold with anhydrous benzene, ethyl acetate, and methyl acetate successively, and then with hot methyl acetate and alcohol. Most of the precipitate dissolved in the methyl acetate when treated in the cold. Ethylglycine hydrochloride, with a m.p. of 145° (soluble in water, positive ninhydrin reaction and negative anhydride reaction), was recovered by precipitation with absolute ether from the solution produced by treatment with hot methyl acetate. Precipitation of the solution produced by treating the precipitate with alcohol likewise yielded ethylglycine hydrochloride. Each of

he filtrates secured in the cold processing of the precipitate, viz.; the ether benzene, ethyl acetate, and methyl acetate filtrates, was concentrated separately to small volume by gently heating it in vacuum. The resultant solutions were precipitated with absolute ether, the precipitates being filtered out, washed with ether, and dried in vacuum desiccators. The melting points of these substances were as follows: 120-130° for the precipitate secured from the ether filtrate; 123° from the ethyl acetate filtrate; 123° from the benzene filtrate; and 120° from the methyl acetate filtrate. The properties of the deposit left after all the processings (positive anhydride and negative ninhydrin reactions, 23.96% total nitrogen, and crystalline form under the microscope) proved that it was diketopiperazine.

All the precipitates were combined and recrystallized from hot chloroform. M.p. 137°. The substance fused at 138° after still another recrystallization from water and drying in a vacuum desiccator. Properties: freely soluble in hot water and chloroform; sparingly soluble in cold water, benzene, or ether; positive anhydride reaction; negative ninhydrin and biuret reactions. It contained no halogen.



(VIII)

The substance is the N,N'-exo-diethoxyoxalyldihydrate-2,5-diglycylethyl ester of dihydropyrazinamidine (VIII; R = C_2H_5).

Found %: C 45.95; H 6.25; N 10.62 (Kjeldahl); M 500 (Rast).
$C_{20}H_{32}O_{12}N_4$. Computed %: C 46.15; H 6.15; N 10.76; M 520.

Determination of oxalic acid by the permanganometric method (after hydrolysis). Found: 49.05 mg; computed: 47.92 mg.

Nothing was found in the ether solution of the first precipitate. Inasmuch as we never secured ethyloxalyldiglycine when we carried out this reaction (with 4 moles of ethylglycine), but recovered large quantities of diketopiperazine, finding that the chlorine in the N,N'-dichloroxalyl-diketopiperazine was replaced by an ethoxy group, the principal reaction involving the formation of an acylamino ester must also involve the inductive cyclization of the excess ethylglycine added, an alcohol being produced. And this alcohol is the source of the substitution of an ethoxy group for the chlorine.

We ran an analogous experiment, but using methylglycine this time, in order to check this assumption of ours. 30 ml of absolute ether was added to 1.5 g of dichloroxalyl-diketopiperazine, chilled with ice and stirred mechanically, and 1.8 g (4 moles) of methylglycine was added. After the mixture had been stirred for 30 minutes, the precipitate that settled was filtered out and washed with ether. The ether was driven out of the ether filtrate in vacuum, leaving behind an oil with the odor of a base, which quickly cyclized into diketopiperazine. The precipitate was treated with acetone. The acetone-insoluble substance was identified as diketopiperazine. The solvent was driven out of the acetone solution in vacuum. The substance that remained was dissolved in chloroform. The undissolved portion (diketopiperazine) was filtered out, while the chloroform solution was evaporated in vacuum to small volume without the application of any

heat and then precipitated with abs ..e ether. The precipitate was filtered out, washed with absolute ether, and dried in a vacuum desiccator. M.p. 153°. Properties: insoluble in water; freely soluble in acetone or chloroform; positive anhydride and negative ninhydrin reactions; negative Beilstein test. The synthesized substance was N,N'-exo-dimethoxyoxalyldihydrate-2,5-diglycylmethyl ester of dihydropyrazinamidine (VIII, R = CH_3).

Found %: C 41.23; H 5.18; N 11.34 (Kjeldahl); M 452 (Rast). $C_{16}H_{24}O_{12}N_4$. C41.38; H 5.17; N 11.55; M 464.

Condensation of N,N'-dichloroxalyl-diketopiperazine with 6 moles of ethyl glycine. 2.1 g (4 moles) of ethylglycine in absolute ether was added, with mechanical stirring and chilling to -10°, to 1.5 g of N,N'-dichloroxalyl-diketopiperazine in 30 ml of absolute ether. The medium was an acid one after all the ester had been added. Without interrupting the chilling or the stirring, another 1.05 g (2 moles) of ethylglycine was added to make the medium a neutral one. The resultant precipitate was filtered out and washed with absolute ether. The ether filtrate was concentrated in vacuum to dryness. Traces of diketopiperazine (a few crystals) were detected in the residue. The precipitate was treated successively with benzene and chloroform in the cold. No individual compound was isolated by driving off the solvent from the benzene filtrate. The chloroform solution was evaporated in vacuum to small volume, and the resulting precipitate was filtered out, washed with absolute ether, and dried in a vacuum desiccator. M.p. 138°. A fusion test of a test sample mixed with the previously synthesized diexo-N-ethoxydioxalyl-ethylglycinehydrate-2,5-dihydropyrazinamidine exhibited no depression.

Found %: N 10.68 (Kjeldahl). $C_{20}H_{32}O_{12}N_4$. Computed %: N 10.76.

The precipitate remaining after the processing with benzene and chloroform was treated with absolute ethyl alcohol. The alcoholic filtrate was precipitated with ether, and the precipitated substance was filtered out, washed with ether, and dried. Its melting point (145°) indicated that it was ethylglycine hydrochloride. The residue that did not dissolve in the absolute alcohol was identified as diketopiperazine. This same experiment was repeated with the same quantities of initial substances and the same sequence of operations, with merely the addition of an excess of 1 g of ethylglycine after the ether medium had been rendered neutral. Stirring for 20 minutes caused the medium to display an alkaline reaction. The precipitate that formed was filtered out, while a current of anhydrous hydrogen chloride was passed through the ether filtrate. The precipitated hydrochloride was filtered out, washed with ether, and recrystallized by precipitating it from absolute alcohol with ether. The substance had a m.p. of 142° after being dried in a vacuum desiccator. No amino nitrogen was found in a Wilstätter titration. A fusion test mixture of the substance with diethyldiglycine-dihydropyrazinamidine hydrochloride exhibited no depression.

SUMMARY

1. A set of reactions is proposed for the rearrangement of acyl amidine derivatives by the action of free amines and amino acids (acylation of amino acids by 5-acylimidazole derivatives), this reaction sequence being corroborated by the formation of ethylglycyl-dihydropyrazinamidine from the latter's oxalyl derivative and ethylglycine.

2. A new scheme is set forth for the formation of glycinamidine by reacting diketopiperazine, oxalyl chloride, and an excess of ethylglycine (more than 4 moles). The scheme has been confirmed experimentally. The correction involved is based upon a more detailed breaking down into stages of the compounds secured in this reaction. The following compounds have been secured and identified:

1. N,N'-dichloroxalyl-diketopiperazine (II); 2. N,N'-exo-dichloroxalyldihydrate-2,5-ethyldiglycine-dihydropyrazinamidine (VII); 3. Di-exo-ethoxyoxalyl-ethylglycinehydrate-2,5-dihydropyrazinamidine (VIII; R = C_2H_5); and 4. Di-exo-N-methoxyoxalyl-methylglycine-2,5-dihydropyrazinamidine (VIII; R = CH_3).

3. Reacting ethylglycine with an exo-acylated amidine yielded the previously synthesized glycinamidine, at the same time rearranging the acyl group to the reacting ethylglycine, thus explaining the chemism of the acylation of imidazole derivatives by primary amines.

LITERATURE CITED

[1] N.I Gavrilov and L.N.Akimova, J.Gen.Chem. 21, 294 (1951).

[2] M.Bergmann, L.Zervas, Z. phys. Chem. 175, 145 (1928).

[3] N.I.Gavrilov and L.N.Akimova, J.Gen.Chem. 17, 2101 (1947).

[4] O.Fischer, Ber., 31, 609 (1898).

[5] H.Staudinger, Ber., 41, 3558 (1908); 42, 3966 (1909).

[6] Shemyakin and Elkina, J.Gen.Chem. 11, 350 (1941); 13, 164, 169, 301 (1943).

[7] L.N.Akimova, N.I.Gavrilov, and N.D.Zelinsky, J.Gen.Chem. 18, 948 (1948).

[8] Bornwater, Chem. Zentr., 1911, II, 441; R. 31, 109.

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RESEARCH ON THE STRUCTURE AND PROPERTIES OF CELLULOSE AND ITS ESTERS

XXXII. THE CONDITIONS GOVERNING THE CONVERSION OF PREPARATIONS OF NATURAL CELLULOSE INTO THOSE OF HYDRATED CELLULOSE AND VICE VERSA

M. Ginsberg and Z. Rogovin

Two structural modifications of cellulose: natural and hydrated cellulose, have been known for a long time. Preparations of hydrated cellulose are secured from natural cellulose under the following circumstances: a) dissolving the cellulose and then recovering it from solution; b) reacting concentrated alkalies with cellulose and then decomposing the resultant alkaline cellulose (especially at low decomposition temperatures); c) esterification and then saponification of the cellulose esters; d) mechanically grinding the cellulose. The formation of new structural modifications of hydrated cellulose involves structural transitions as well as changes in the physical and chemical properties of preparations of natural cellulose. The X-ray photograph of the cellulose changes, and the adsorptive capacity, the hygroscopicity, and the coloring capacity of the cellulose material increase, as does the solubility of the cellulose itself and of its esters [1]. Hence, the structural changes caused in cellulose preparations during various operations and processings are paralleled as a rule, by changes in the physico-chemical properties of these products. Up to the present time it has been accepted that the structural changes in natural cellulose that result in the formation of a new modification – hydrated cellulose – are always accompanied by changes in the physico-chemical properties of these materials. There is no foundation, however, for such a generalization. As we have succeeded in demonstrating, it is possible to effect the interconversions of these structural modifications of cellulose under such conditions as to prevent the changes in the X-ray picture and the physico-chemical properties of the cellulose from occurring simultaneously. In the production of alkaline cellulose under special conditions and in its subsequent saponification, for example, we can secure cellulose preparations that possess the structure of hydrated cellulose, but whose physico-chemical properties are not perceptibly different from those of preparations of natural cellulose. On the other hand, heating a hydrated cellulose preparation to high temperature in glycerol yields preparations whose structure is that of natural cellulose, but whose physico-chemical properties are the same as those of a hydrated cellulose. The results obtained in our research on this problem, which are, we believe, of definite interest in the investigation of the mechanism governing the mutual interconversion of these structural modifications, are set forth in the present paper.

We employed the following research methods to identify the properties of preparations of natural and hydrated cellulose.

1) Determining the structural changes by means of X-ray analysis. As we know, the structural changes occurring during the transition from natural to

hydrated cellulose involve a change in the configuration (a reciprocal reversal) of individual units in the cellulose macromolecule [2], with corresponding changes in the cellulose X-ray picture [3].

2) The physico-chemical changes in the properties of these esters were identified by means of the following indexes.

a) The change in the sorption of moisture by the cellulose materials; the kinetics of sorption and desorption of moisture by the preparations tested, as well as the total moisture sorbed by these preparations were measured by investigating the sorption process in high vacuum with a McBain-Baker balance at moisture contents ranging up to 75%.*

b) The change in the intensity of the color imparted to these materials when colored under identical conditions; the dyeing intensity is to a certain extent governed by the magnitude of the internal active surface of the material and mainly depends upon the nature and the intensity of the reactions between the individual macromolecules or their component units (the existence of mutual saturation of the regular sections of the fiber in which there is no diffusion of the dye).

We determined the amount of dye sorbed by the procedure worked out by Sokolov [4]. This method involves the treatment of the cellulose with a substantive dye (direct blue) for 5 minutes at the boiling point. Then the excess dye is washed out, and the dyed material is dried. 0.1 g of the dyed fiber is hydrolyzed with concentrated H_2SO_4, and the quantity of dye in the solution is determined colorimetrically.

c) Differences in the resistance of preparations of natural and hydrated cellulose to the action of dilute acids at high temperatures are some indication of changes in their reactivity. As Losinsky [5] was the first to demonstrate, followed by Sharkov [6], preparations of hydrated cellulose that are regenerated from alkaline cellulose are less resistant to the action of dilute acids and therefore are hydrolyzed more rapidly. To ascertain the resistance of these cellulose preparations to hydrolysis we determined the so-called hydrolysis difference between the preparations, that is, the increase in the iodine number (characterizing the number of ruptured glucoside bonds) produced by processing the cellulose for 15 minutes with 5% H_2SO_4 at 100° [7].

Our preliminary investigations indicated that the change in the X-ray photos is paralleled by a change in the physico-chemical properties of hydrated cellulose preparations that had been regenerated from alkaline cellulose, which in turn had been prepared under the customary conditions by the action of concentrated aqueous solutions of an alkali upon cellulose.

As we know, during the process of mercerization the X-ray photograph changes as a result of the formation of alkaline cellulose and the production of hydrated cellulose when the former product is decomposed, with nothing but 14-18% solutions of NaOH acting upon the cellulose. When cellulose is treated with caustic soda solutions of lower concentration, no alkaline cellulose, such as is characterized by obvious changes in the X-ray photos, is produced.

The colorability and the hydrolysis difference of preparations of regenerated cellulose are changed appreciably only in the case of those preparations that are produced by the action upon cellulose of NaOH solutions of such concentration as yield the clear X-ray picture of an alkaline cellulose. Table 1 gives the data on the effect of the NaOH concentration used for mercerizing upon the change in the X-ray picture of the cellulose during the formation of alkaline cellulose and upon the physico-chemical properties of the hydrated cellulose regenerated from the alkaline cellulose.

*The kinetics of sorption were measured by Kh. U. Usmanov, to whom we are indebted.

Whenever the production of an alkaline cellulose does not entail appreciable swelling, the change in the structure of the cellulose does not involve an appreciable parallel change in its physico-chemical properties. A cellulose preparation regenerated from cellulose trialcoholate is a typical example of this type of transformation. This product is secured by reacting the cellulose with a solution of metallic sodium in liquid ammonia under such conditions as to prevent any appreciable swelling of the cellulose. The indexes of the properties of a cellulose regenerated from the cellulose trialcoholate are compared with those of preparations of natural and hydrated cellulose in Table 2.

TABLE 1

NaOH concentration during mercerizing, grams/liter	0	45.2	106.2	145.3	174.4	250	362	538
The X-ray picture of alkaline cellulose appears after mercerization	No	No	No	Yes	Yes	Yes	Yes	Yes
The X-ray picture of hydrated cellulose appears after decomposition of the alkaline cellulose	No	No	No	Yes	Yes	Yes	Yes	Yes
Magnitude of the hydrolysis difference	0.26	0.23	0.33	0.51	1.38	1.44	1.45	1.43
Colorability (grams of dye per 100 grams of cellulose)	1.54	1.54	1.53	2.02	2.20	2.18	-	2.24

TABLE 2

Preparation	Type of X-ray picture	Colorability (g of dye per 100 g cellulose)	Percent sorption of moisture at 75% moisture content	Hydrolysis difference
Natural cotton cellulose.....	Natural cellulose	1.54	9.3	0.25
Cellulose regenerated from alkaline cellulose produced by reacting cellulose with an 18% solution of NaOH	Hydrated cellulose	2.25	12.4	1.45
Cellulose regenerated from cellulose trialcoholate.....	Hydrated cellulose	1.80	11.6	0.84

As we see from these data, the structure of a cellulose regenerated from cellulose trialcoholate (insofar as it can be defined from an X-ray picture) does not differ from that of hydrated cellulose formed by hydrolyzing an alkaline cellulose produced under ordinary conditions. The chemical properties of this cellulose preparation differ from those of the hydrated cellulose, however, occupying a position halfway between preparations of natural and hydrated cellulose.

The cellulose regenerated from an alkaline cellulose with $\gamma = 95$, produced by the action of a 3% solution of NaOH in isoamyl alcohol under conditions that practically exclude any swelling of the cellulose, is practically identical with natural cellulose, in structure as well as in physico-chemical properties. No

change in the X-ray picture of natural cellulose occurs in these preparations. This is apparently due to the relatively low degree of substitution of the OH groups in the cellulose macromolecule when alkaline cellulose is produced under these conditions.

Cellulose preparations produced by heating hydrated cellulose to 240° in glycerol are examples of a change in the physico-chemical properties of natural cellulose without any change in its structure. As has been shown by Kubo [8], Meyer [9], and Mikhailov, Kargin, and Elinek [10], the X-ray picture of a hydrated cellulose vanishes when various preparations of hydrated cellulose are heated to 140-300° in glycerol, in water under pressure, or in other liquids that cause swelling, the clear X-ray picture of a natural cellulose taking its place. A partial structural modification of natural cellulose, but not of hydrated cellulose, occurs whenever the regeneration of the cellulose and of its esters is effected at high temperature (60-80°). This has been established for celluloses regenerated at high temperatures from cellulose nitrate, acetylcellulose, and cellulose xanthogenate. Hence, preparations of hydrated cellulose can be converted into a structural modification of natural cellulose by heating them in a medium that causes swelling. But we still do not know whether this conversion is accompanied by corresponding changes in the physico-chemical properties of these preparations. To clear this matter up, we heated cotton cellulose, regenerated from alkaline cellulose, in glycerol at 230° for one hour and then investigated the properties of the different preparations. The results are listed in Table 3.

TABLE 3

Preparation	Type of X-ray picture	Percent sorption of moisture at 75% moisture content	Colorability, (g of dye per 100 g of cellulose)	Hydrolysis difference
Natural cellulose	Natural cellulose	9.3	1.52	0.25
Hydrated cellulose	Natural cellulose	12.4	2.25	1.52
Hydrated cellulose, heated in glycerol at 230°	Largely coincides with X-ray of natural cellulose	11.2	2.25	1.60

As we see from these data, the physico-chemical changes that take place in cellulose preparations in the transition from a modification of natural cellulose to hydrated cellulose and due, apparently, to the rupture of the stabler bonds between the macromolecules of natural cellulose [1] are, by and large, irreversible. The shift from a structural modification of hydrated cellulose to a modification of natural cellulose is not accompanied by a simultaneous change in the physico-chemical properties of these preparations. Hence, we can secure preparations of cellulose that possess the structure of natural cellulose and the properties of hydrated cellulose.

It should be noted that the indexes listed in Table 3 do not give a complete picture of the differences in the properties of these cellulose modifications. As has been demonstrated recently, there are other differences between

TABLE 4

Comparative Properties of Various Structural Modifications of Cellulose Preparations

Material	Conditions of preparation	Type of X-ray picture	% sorption of moisture, at 75% moisture content	Colorability	Rate of hydrolysis by mineral acids	Rate of acetylation of the dried fiber [12]	Integral heat of wetting cal/mole	Fiber strength after processing with organic solvents [12]
Natural cellulose	Biochemical synthesis of cellulose	Natural cellulose	9-9.5	Less than for preparations (3) and (4)	Less than for preparations (3) and (4)	Higher than for preparations (3) and (4)	10	Drops
Cellulose 1	Regeneration of cellulose from compounds with $\gamma > 150$, produced with negligible swelling	Hydrated cellulose	10.5-11	The same	The same	?	?	?
Hydrated cellulose	Regeneration of cellulose from various compounds	Hydrated cellulose	12-12.5	Higher than for preparations (1) and (2)	Higher than for preparations (1) and (2)	Less than for preparations (1) and (2)	15-22	Rises
Cellulose 2	Heating hydrated cellulose in glycerol to 200-250°	Coincides by and large with the X-ray of natural cellulose	11-12.5	The same	The same	?	?	?

preparations of natural cellulose and hydrated cellulose, namely, the nature of the change in the fiber strength during swelling in organic liquids [11], the rate of acetylation of the dried fiber [12], etc. Ascertaining the changes occurring in these properties in new structural modifications of cellulose requires further research.

In view of the data cited, we consider it desirable to supplement the existing classification of cellulose preparations into modifications of natural and hydrated cellulose and to distinguish cellulose preparations that occupy an intermediate position between these two modifications (Table 4).

As has been stated already, heating preparations of hydrated cellulose to high temperature in glycerol does not result in complete reduction of the more stable bonds between the macromolecules, present in preparations of natural cellulose and ruptured during the formation of cellulose esters. Apparently, these bonds are formed, in part, when the cellulose is regenerated from solutions, however. The reduction of a small number of these bonds has no perceptible effect upon any changes in the physico-chemical properties of preparations of hydrated cellulose, though they do cause a considerable change in the solubility of the

resultant cellulose derivatives. Further research on this problem is of considerable interest.

SUMMARY

1. An investigation has been made of the conditions governing the formation and the reciprocal transition of two structural modifications of cellulose – natural cellulose and hydrated cellulose.

It has been shown that a change in the structure of cellulose materials is not always paralleled by changes in their physico-chemical properties when preparations of natural cellulose are converted into hydrated cellulose, and vice versa.

2. When cellulose is regenerated from a cellulose trialcoholate, prepared by reacting cellulose with a solution of metallic sodium in liquid ammonia, we get a cellulose preparation that has the structure of hydrated cellulose, though its physico-chemical properties occupy an intermediate position between preparations of natural and hydrated cellulose.

3. Heating hydrated cellulose to 230° in glycerol causes a structural change of the hydrated cellulose into a modification of natural cellulose. The physico-chemical properties of these preparations are, however, basically the same as those of preparations of hydrated cellulose.

LITERATURE CITED

[1] Rogovin, High-Molecular Compounds, No. 9 (1949).

[2] Kargin and Leipunskaya, J.Phys.Chem. 14, 312 (1940); 15, 1011 (1941).

[3] Paper by Katz in Hess's book: The Chemistry of Cellulose and Its Associates, p. 402. State Chemical Technology Press (1934).

[4] Sokolov, Trans. Fourth Conf. on Chemistry of Aniline Dyes, p. 88 (1939); Osipova and Rakhlina, Textile Industry, No. 8 (1948).

[5] Lozinsky, Wood Industry Herald, No. 21, 197 (1906).

[6] Sharkov, Hydrolysis Industry, Vol. I, p. 149-150.

[7] Rogovin and Makarova-Zemlyanskaya. Controlling the Production of Rayon, p. 76.

[8] Kubo, Kolloid Z., 93, No. 3, 338 (1940); 96, No. 1, 41 (1941).

[9] Meyer and Badenhinzen. Nature, 140, 281 (1937).

[10] Mikhailov, Kargin, and Elinek. Researches on High-Molecular Compounds, 285. USSR Acad.Sci.Press (1949).

[11] Lauer, Kolloid Z., 107, No. 2, 43 (1944).

[12] Staudinger, Dohle, Henk, J. prak. Chem., 161, 191 (1942); Rogovin and Sverdlin, J.Appl.Chem. 12, 1170 (1939).

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ABSORPTION SPECTRA AND STRUCTURES OF BENZENE DERIVATIVES

XV. 3-HYDROXY- AND 3-METHOXYACETOPHENONE*

N. A. Valyashko and A. E. Lutsky

N.A.Valyashko and Yu.S.Rozum [1] have made a spectrographic study of the 2- and 4-hydroxyacetophenones and their esters; the present paper sets forth the results of a spectrographic investigation of 3-hydroxyacetophenone and its methyl ester.

Syntheses. 3-Hydroxyacetophenone was synthesized from acetophenone, converting it into the 3-nitro, 3-amino, and 3-hydroxy derivatives. The acetophenone was nitrated with a mixture of potassium nitrate and sulfuric acid. 15 g of freshly distilled acetophenone was added drop by drop, with stirring, to 105-120 g of sulfuric acid (sp. gr. 1.84). A chilled solution of KNO_3 in H_2SO_4 of the same concentration was added drop by drop, with vigorous mechanical stirring, to the chilled mixture. The rate at which the solution was added was so adjusted as to keep the temperature of the reaction mixture below -10°. Stirring and chilling were continued for 30 minutes after all the solution had been added; then the mixture was sprayed in a fine jet over crushed ice. The light-yellow crystals of 3-nitroacetophenone were suction-filtered, washed with water, and desiccated. Yield: 82-86.5%. M.p. 75-76° (after a single crystallization from alcohol).

The 3-nitroacetophenone was reduced to 3-aminoacetophenone as follows: a solution of 30 g of 3-nitroacetophenone in 60 ml of ethyl alcohol was added, with vigorous mechanical stirring, to 50 g of iron filings suspended in a solution of 10 ml of glacial acetic acid in 200 ml of water. Stirring was continued for another 20 minutes after this addition was complete; then the reaction mixture was boiled with water for about an hour and filtered while hot. The precipitate on the filter and in the reaction vessel was boiled two more times with fresh batches of water to prevent any loss of the 3-aminoacetophenone. The crystals of 3-aminoacetophenone that settled out of the filtrates were suction filtered, and the mother liquor was alkalinized; alcohol was used to extract some more 3-aminoacetophenone from the precipitate thrown down by this alkalinization. The yield of 3-aminoacetophenone totaled 80%; its m.p. was 92-92.5°. The 3 aminoacetophenone was diazotized, and the diazonium compound was converted into 3-hydroxyacetophenone by the methods specified by Fuson [2] and Rupe and Mayewski [3]. The synthesized 3-hydroxyacetophenone was purified by triple recrystallization from hot water; it was a white, fluffy mass, with a m.p. of 96° (Bidginelli [4] gives the m.p. as 92-93°; Fuson [2] gives 94-94.5°; Pfeiffer [5] and Rupe and Mayewski [3] give 95-96°; and Besthorn [6] and Meyer and Jacobson [7] give 96°), freely soluble in water and in alcohol, sparingly

*Extract from the candidate's dissertation of A. E. Lutsky, defended in 1940 in the S. M. Kirov Institute of Chemical Technology, Kharkhov.

soluble in hexane. The 3-methoxyacetophenone was synthesized from 3-hydroxyacetophenone by methylating it with dimethyl sulfate as outlined by Auwers [8] and then purifying it by distillation in vacuum. It was a colorless liquid with a b.p. of 130-131° (15 mm), freely soluble in water, alcohol, hexane, and concentrated sulfuric acid.

Spectrographic Analyses

Tasaki [9] investigated the ultraviolet absorption of 3-hydroxyacetophenone, but all he says is that its curve resembles that of unsubstituted acetophenone. No spectrographic analysis has been made of 3-methoxyacetophenone up to the present time. We made a quantitative analysis of both of these compounds in hexane and in ethyl alcohol, as well as in alcoholic solutions of alkalies and of sulfuric acid, in concentrated sulfuric acid, and in sulfuric acid diluted with water.

3-Hydroxyacetophenone in Hexane and in Ethyl Alcohol

Owing to the sparing solubility of 3-hydroxyacetophenone in hexane, it can only be investigated in this solvent at concentrations below 10^{-3} m. The absorption curve in hexane (Table 1 and Fig. 2, Curve 2) begins at λ = 3530 A and ε = 100 and rises to a maximum at λ = 3035 A and ε = 6000. At the maximum this curve

TABLE 1

3-Hydroxyacetophenone in hexane, 10^{-3} to $2\cdot10^{-5}$ mol.			3-Hydroxyacetophenone in alcohol, 10^{-2} to $2\cdot10^{-5}$ mol.		
λ		ε	λ		ε
3530		100	3660		10
3050		5000	3460		250
3035	maximum	6000	3140		4000
3020		5000	3110	maximum	5000
2740		500	3080		4000
2725	minimum	400	2770		500
2710		500	2750	minimum	400
2460		12500	2730		500
2450	maximum	15000	2545		9000
2440		12500	2525	maximum	10000
2300		5000	2510		9000
2285	minimum	4000	2360		3500
2270		5000	2340	minimum	3000
2140		30000	2325		3500
2125	maximum	35000	2200		20000
2110		30000	2180	maximum	25000
2080		20000	2160		20000
			2105		12500

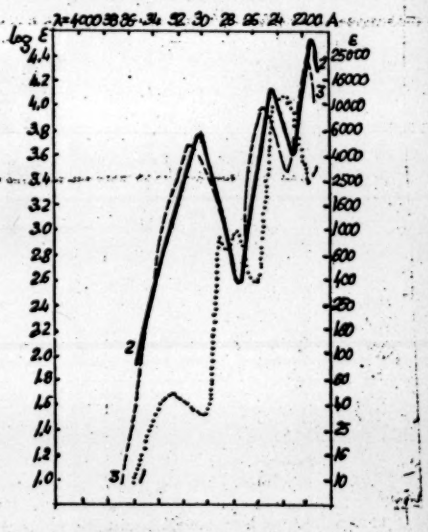


Fig. 1. 1) Acetophenone, 10^{-2} to 10^{-5} mole in hexane; 2) 3-hydroxyacetophenone, 10^{-3} to $2\cdot10^{-5}$ mole in hexane; 3) 3-hydroxyacetophenone, 10^{-2} to $2\cdot10^{-5}$ mole in alcohol.

is rounded off, forming a broad α_2 band, and then drops to its first minimum at λ = 2725 A and ε = 400; the absorption curve then rises steeply to its second maximum at λ = 2450 A and ε = 15000 with a narrower α_1 band; the curve possesses another minimum in the far ultraviolet at λ = 2285 A and ε = 4000 and a third maximum with an extremely intense α_1' band at λ = 2125 A and ε = 35000.

In ethyl alcohol, we investigated the absorption in solutions with concentrations of 10^{-2}, 10^{-3}, 10^{-4}, and $2 \cdot 10^{-5}$ mol. As in hexane, the absorption curve consists of 3 bands: α_2, α_1, and α_1' (Table 1 and Fig. 1, Curve 3). The curve begins at $\lambda = 3660$ A and $\varepsilon = 10$, rises rather steeply, and crosses the curve for 3-hydroxyacetophenone in hexane at $\lambda = 3490$ A and $\varepsilon = 160$. At values of below 160 the absorption curve in alcohol is shifted somewhat toward the shorter wavelengths, compared to the hexane curve (the shift amounting to 20 A at ε = 100); above 160, on the other hand, the curve in alcohol is shifted somewhat toward the longer wavelengths, compared to the curve in hexane. In alcohol, moreover, the maxima and minima of all the bands are shifted toward the longer wavelengths, viz.: the maxima of the α_2 and α_1 bands by 75 A and the maximum of the α_1' band by 55 A: the first minimum is shifted by 25 A, and the second by 55 A. We also observe a considerable decrease in the intensity of absorption (by a factor of 12.5 to 1.5).

The data on the band maxima for 3-hydroxyacetophenone are tabulated in Table 2 together with the corresponding data for acetophenone reported by N.A. Valyashko and Yu.S.Rozum [10] and Ley and Winghen [11] for acetophenone, for 3-hydroxybenzaldehyde reported by N.A.Valyashko and M.M.Shcherbak [12], and for benzaldehyde reported by Ley [13]

TABLE 2

Compound	α_2 Band		φ Band		α_1 Band		α_1' Band	
	λ	ε	λ	ε	λ	ε	λ	ε
Acetophenone in hexane	3250	50	2865 2770	800 1000	2370	13000	–	–
3-Hydroxyacetophenone in hexane ...	3035	6000	Not manifested		2450	15000	2125	35000
Acetophenone in alcohol	3210	50	2770	1000	2420	12500	1990	20000
3-Hydroxyacetophenone in alcohol ..	3110	5000	Not manifested		2525	10000	2180	25000
Benzaldehyde in alcohol	3280	20	2805	1630	2440	16260	–	–
3-Hydroxybenzaldehyde in alcohol	3180	3500	Not manifested		2550	10000	2200	20000

As we see in Table 2 and Fig. 1, the absorption of acetophenone is changed somewhat by introducing a hydroxyl group in the meta position to the carbonyl group, viz.: a) the maximum of the longwave band (α_2) of 3-hydroxyacetophenone is 215 A farther toward the shorter wavelengths of the spectrum in hexane, and 100 A farther in alcohol, than for unsubstituted acetophenone; the intensity of these bands is very much greater in 3-hydroxyacetophenone (120 and 100 times, respectively); b) the φ band of acetophenone is not manifested on the 3-hydroxyacetophenone curve, neither in alcohol nor in hexane; c) in 3-hydroxyacetophenone the α_1 and α_1' bands of acetophenone, in contrast to the α_2' band, are shifted toward the longer wavelengths (by 105 and 190 A in alcohol), though the change in intensity is rather slight. This influence of the hydroxyl group in a meta position to the carbonyl group is, apparently, a general phenomenon. It is found not only in acetophenone, but in benzaldehyde as well. In the latter, the addition of a hydroxyl group at the meta position causes the same quantitative as well as qualitative changes in the absorption curve of the original benzaldehyde as were found in acetophenone (Table 2).

Comparing these figures with the data cited by N.A.Valyashko and Yu.S.Rozum for 2-hydroxyacetophenone [1] indicates that the effect of a hydroxyl group in

the 3-position to the carbonyl group resembles that of the same group in the 2-position, differing from the effect of the hydroxyl group in the 4-position. Whereas the absorption is greatly increased in 4-hydroxyacetophenone in the φ band of acetophenone, the absorption is increased in the α_2 band of acetophenone for 3-hydroxyacetophenone and 2-hydroxyacetophenone, this increase being considerable (in hexane). In the 3-hydroxyacetophenone all we find is a noticeable shift of the maximum of this band toward the shorter wavelengths (by 215 A) and the failure of the φ band to appear, due, apparently, to an even greater drop in its intensity than was the case in the 2-hydroxyacetophenone. Some singularities of 3-hydroxyacetophenone insofar as the effect of the solvent upon its absorption is concerned should be mentioned. Changing from hexane to ethyl alcohol causes a drop in the intensity of the absorption bands in 3-hydroxyacetophenone, in contrast to the behavior of 2-hydroxyacetophenone, and a pronounced shift of the α_2 band maximum toward the longer wavelengths (in 2-hydroxyacetophenone, the position of the maximum remains unchanged, while the intensity is increased).

The data in Table 1 yield still another conclusion. Changing from hexane to alcohol produces a shift of the α_1 band toward the longer wavelengths of about the same magnitude for 3-hydroxyacetophenone as for the unsubstituted acetophenone. A different situation obtains with regard to the α_2 band. In 3-hydroxyacetophenone this band is shifted toward the longer wavelengths, while in acetophenone it is shifted, on the contrary, to the shorter wavelengths. This is evidence that the α_2 band in 3-hydroxyacetophenone arises from a different cause than in the unsubstituted acetophenone. The fact that the long-wavelength boundary of the α_2 band in 3-hydroxyacetophenone is shifted toward the shorter wavelengths in the region below $\varepsilon = 160$, while it shifts toward the longer wavelengths above 160, when we change from hexane to alcohol, indicates the complexity of this band.

3-Methoxyacetophenone in hexane and in ethyl alcohol. We investigated 3-methoxyacetophenone in hexane solutions of the following concentrations: 10^{-2}, 10^{-3}, and $4\cdot10^{-5}$ mol. The absorption curve (Table 3 and Fig. 2, Curve 2) starts at $\lambda = 3550$ A and $\varepsilon = 10$. The curve rises, exhibiting a clearly marked bend between 3450 and 3340 A and $\varepsilon = 30$-40, parallel and corresponding to the α_2 band of acetophenone at $\lambda = 3250$ A and $\varepsilon = 50$; after this bend the curve rises steeply to its first maximum at $\lambda = 3025$ A and $\varepsilon = 6000$. After dropping to a deep minimum at $\lambda = 2650$ A and $\varepsilon = 130$, the curve rises steeply again, exhibiting an intense α_1 band with a maximum at $\lambda = 2490$ A and $\varepsilon = 12500$. There is another narrow band (α_1') in the shortwave ultraviolet, with a maximum at $\lambda = 2145$ A and $\varepsilon = 30000$. The minimum separating the α_1 from the α_1' band is located at the following concentrations: 10^{-3}, 10^{-4}, and $6\cdot10^{-5}$ mol. The absorption curve (Table 3 and Fig. 2, Curve 3) starts at $\lambda = 3450$ A and $\varepsilon = 100$, rises steeply, and exhibits an α_2 band, with a maximum at $\lambda = 3085$ A and $\varepsilon = 3500$. As in hexane, the curve exhibits two more bands: α_1, with a maximum at $\lambda = 2490$ A and $\varepsilon = 7000$, and α_1', with a maximum at $\lambda = 2185$ A and $\varepsilon = 16600$. The minima separating the α_2 from the α_1 band, and the α_1 from the α_1' band are located at $\lambda = 2735$ A and $\varepsilon = 400$ and $\lambda = 2320$ A and $\varepsilon = 1600$, respectively.

When we change from hexane to alcohol as the solvent, no change occurs in the nature of the absorption of 3-methoxyacetophenone, as may be seen from inspection of the curves. The only changes, as in the case of 3-hydroxyacetophenone, are shifts of the longwave portion of the absorption curve and of the maxima and minima of all the bands toward the longer wavelengths (the shift being 60 A in the α_2 band, 30 A in the α_1 band, and 40 A in the α_1' band), and with a marked decrease in the intensity of absorption (by a factor of 1.6 to 1.8). Table 4 lists the figures for the band maxima of 3-hydroxy- and 3-methoxyacetophenone in hexane and in alcohol. We see from the absorption curves of

TABLE 3

3-Methoxyacetophenone in hexane, 10^{-2} to $4 \cdot 10^{-5}$ mol.			3-Methoxyacetophenone in alcohol, 10^{-3} to $6 \cdot 10^{-5}$ mol		
λ		ε	λ		ε
3550		10	3450		100
3470		25	3130		3000
3450		30	3085	maximum	3500
3380		35	3040		3000
3340		40	2760		500
3330		50	2735	minimum	400
3060		5000	2710		500
3025	maximum	6000	2520		6000
2990		5000	2490	maximum	7000
2670		160	2460		6000
2650	minimum	130	2340		2000
2630		160	2320	minimum	1600
2480		10000	2300		2000
2460	maximum	12500	2200		13300
2440		10000	2185	maximum	16600
2300		3500	2170		13300
2290	minimum	3000	2150		11660
2280		3500			
2170		25000			
2145	maximum	30000			
2120		25000			
2090		17500			

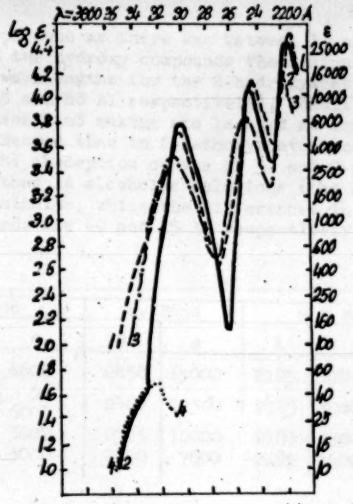


Fig. 2.
1) 3-Hydroxyacetophenone, 10^{-3} to $2 \cdot 10^{-5}$ mol. in hexane; 2) 3-methoxyacetophenone, 10^{-2} to $4 \cdot 10^{-5}$ mol., in hexane; 3) 3-methoxyacetophenone, 10^{-3} to $5 \cdot 10^{-5}$ mol., in alcohol; 4) α_2 band of acetophenone in hexane.

3-hydroxy-and 3-methoxyacetophenone in hexane, as well as from the measurements of their absorption spectra (Tables 1 and 3), that the transition from a hydroxy to a methoxy compound causes a noticeable shift of the longwave portion of the absorption curve toward the shorter wavelengths (the shift totalling 240 A at $\varepsilon = 100$, and 60 A at $\varepsilon = 1300$), the position of the band maxima remaining practically unchanged. Another distinction between the absorption curves of 3-methoxy and 3-hydroxyacetophenone is the marked lowering of the former's absorption minimum in the φ band of acetophenone. These relationships are somewhat different in alcohol, namely: the shift toward the shorter wavelengths of the longwave boundary of the 3-methoxyphenone band is less in alcohol than in hexane (totalling 60 A at $\varepsilon \approx 100$); the maxima of the α_2 and α_1 bands and their longwave edges are shifted toward the shorter wavelengths (by 25 and 35, respectively); and the intensity of all three bands is diminished considerably.

This effect of esterification upon the absorption of 3-hydroxyacetophenone differs somewhat from the effect of esterification upon 2-hydroxyacetophenone. As N.A.Valyashko and Yu.S.Rozum [1] have discovered, the change from 2-hydroxy- to 2-methoxyacetophenone not only causes a much more pronounced shift of the longwave portion of the curve than takes place during the transition from 3-hydroxy- to 3-methoxyacetophenone, but also a quite considerable shift toward the shorter wavelengths of the band maximum (280 A in α_2, 100 A in α_1 in hexane, and 215 and 55 A, respectively in alcohol. As a result of the large displacement of the absorption curve in the esterification of 2-hydroxyacetophenone there is not as much of a difference in the position of the bands between the

absorption curves of 3- and 2-methoxyacetophenone as there was between 3- and 2-hydroxyacetophenones. Moreover, though in the hydroxy compounds the maximum of the α_2 and α_1 bands are located at longer wavelengths for the 2-hydroxyacetophenone than for the 3-hydroxyacetophenone (215 and 60 A, respectively), conditions are reversed for the methoxy compounds: these band maxima are located at longer wavelengths in the case of 3-methoxyacetophenone than in 2-methoxyacetophenone (55 and 50 A, respectively, in hexane). The absorption curves of 3- and 2-methoxyacetophenones are especially close together in alcoholic solutions (the long-wave portions of both curves practically coincide, while the differences in the position of the maxima in the α_2 and α_1 bands are 40 and 15 A, respectively).

TABLE 4

Compound	α_2 Band		α_1 Band		α_1' Band	
	λ	ε	λ	ε	λ	ε
3-Hydroxyacetophenone in hexane	3035	6000	2450	15000	2125	35000
3-Methoxyacetophenone in hexane	3250* / 3025	50* / 6000	2460	12500	2145	30000
3-Hydroxyacetophenone in alcohol	3110	5000	2525	10000	2180	25000
3-Methoxyacetophenone in alcohol	3085	3000	2490	7000	2185	16000

Figs. 1 and 2 also show that the absorption curve of 3-methoxyacetophenone coincides with the boundary of the α_2 band in hexane, within the limits of experimental error, between ε = 10 and 40. This is evidence of the complexity of the α_2 band of 3-methoxy- (and hence of 3-hydroxy-) acetophenone. It consists of two bands: one of them (α_2') corresponds, as the figure indicates, to the α_2 band of acetophenone, the intensity of this band in 3-methoxyacetophenone being almost the same as that in acetophenone; the maximum of the other band lies in the shorter-wavelength region of the spectrum, its longwave edge touching the first band (we shall call this band α_2' for the sake of convenience). In alcohol the α_2' band (like that of unsubstituted acetophenone) is shifted toward the shorter wavelengths, as is readily seen from a comparison with the curve for 3-hydroxyacetophenone in alcohol, while the α_2" band is shifted toward the longer wavelengths, covering the first band. The hypothesis was advanced above that the α_2 band has a different origin in 3-hydroxyacetophenone than in unsubstituted acetophenone. The absorption curve of 3-methoxyacetophenone in hexane confirms this supposition; it indicates that the α_2 band of the compounds in question is composed of the band of the original acetophenone and of a new, much stronger band (α_2"), due to the presence of hydroxy and methoxy groups in the molecule.

3-Hydroxyacetophenone in alcoholic solutions of sodium alcoholate. We investigated 3-hydroxyacetophenone in alkaline solutions of various concentrations, namely: 10^{-2} to $3\cdot10^{-5}$ mol with one mol of sodium alcoholate, 10^{-3} to $3\cdot10^{-5}$ mol 100 mols of sodium alcoholate, and 10^{-3} to $2\cdot10^{-5}$ mol with 1000 mols of sodium alcoholate per one mol of the hydroxy compound. The presence of one mol of sodium alcoholate in a 10^{-2} molar solution causes a considerable shift of the absorption toward the longer wavelengths, as compared with the absorption observed in a neutral alcoholic solution, as may be seen from an inspection of the absorption curves plotted in Fig. 3. The solution itself is colored an intense yellow. The absorption curve starts at λ = 4250 A and ε = 10, i.e. 590 A farther into the long-wavelength region than in an alcoholic solution containing no alkali. Inasmuch as the presence of an excess of sodium alcoholate has no appreciable effect upon the absorption of unsubstituted acetophenone [10] or of 3-methoxyaceto-

*Assumed.

TABLE 5

3-Hydroxyacetophenone, 10^{-3} to $3 \cdot 10^{-5}$ mols, + 100 mols of sodium alcoholate			3-Hydroxyacetophenone, 10^{-3} to $2 \cdot 10^{-5}$ mol, + 1000 mols of sodium alcoholate		
λ		ε	λ		ε
4070		100	4080		100
3550		4000	3560		3000
3495	maximum	5000	3515	maximum	3500
3440		4000	3470		3000
2990		130	2940		350
2940	minimum	100	2910	minimum	300
2890		130	2880		350
2670		4000	2800		1600
2655	maximum	5000	2790		2000
2640		4000	2760		3000
2600		2500	2730		3500
2590	minimum	2000	2690		4000
2580		2500	2650	extension	5000
2400		26660	2600		6000
2380	maximum	30000	2560		7000
2360		26660	2370		20000
2210		6000	2360	maximum	23300
			2350		20000
			2260		10000
			2230	minimum	9000
			2200		10000
			2190		12500

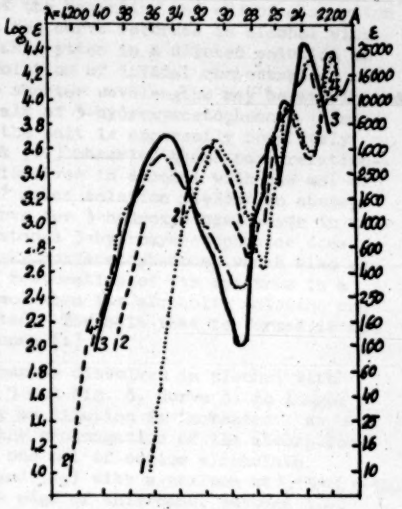


Fig. 3. 1) 3-Hydroxyacetophenone, 10^{-2} to $2 \cdot 10^{-5}$ mol., in alcohol; 2) 3-hydroxyacetophenone, 10^{-2} to $3 \cdot 10^{-5}$ mol., in alcohol + 1 mol. of C_2H_5ONa; 3) 3-hydroxyacetophenone, 10^{-3} to $3 \cdot 10^{-5}$ mol., in alcohol + 100 mols. of C_2H_5ONa; 4) 3-hydroxyacetophenone, 10^{-3} to $2 \cdot 10^{-5}$ mol., in alcohol, +1000 mols. of C_2H_5ONa.

phenone (vide infra), this pronounced shift of the curve for 3-hydroxyacetophenone may be attributed to the formation of a sodium salt. Diluting a 10^{-2} molar solution to a concentration of 10^{-3} mol weakens the color of the solution noticeably. Absorption begins at λ = 3890 A, ε = 100; the curve rises steeply to λ = 3600 A, ε = 1000. In this case the beginning of absorption in the solution with a concentration of 10^{-3} mol does not coincide with the end of absorption in the initial solution with a concentration of 10^{-2} mol, i.e., dilution causes a break in the absorption boundary. Dilution to 10^{-3} mol shifts the curve toward the shorter wavelengths, though, compared to the curve for a neutral alcoholic solution, it is still noticeably shifted toward the longer wavelengths (by 380 A at ε = 100). The absorption curve for a 10^{-3} molar solution with one mol of sodium alcoholate also possesses a band minimum at λ = 2845 A and ε = 4000. As we see from Fig. 3 this minimum is likewise an absorption minimum of 3-hydroxyacetophenone in neutral alcohol (at λ = 2750 A and ε = 400), merely shifted toward the longer wavelengths by the action of the alkali. Evidently, the alkali's action shifts not only the longwave portion, but the whole absorption curve toward the longer wave lengths. Diluting a 10^{-3} molar solution containing one mol of sodium alcoholate to 10^{-4} mol yields an absorption curve whose start does not coincide with the end of absorption for the original concentration either. The curve is shifted toward the shorter wavelengths, nearly coinciding throughout its length with the curve for 3-hydroxyacetophenone in neutral alcohol. As we dilute further to

$5 \cdot 10^{-5}$ mol, we no longer observe a failure of the beginning and end of absorption to coincide. The curve fully coincides with the curve recorded in alcohol with no alkali. The failure of the beginning of absorption in a diluted solution to coincide with the end of absorption in the solution of initial concentration and the consequent shift of the curve toward the shorter wavelengths may be attributed to the alcoholysis of the resulting sodium salt of 3-hydroxyacetophenone. In a solution whose concentration is 10^{-4} molar, the salt is apparently completely alcoholized. N.A.Valyashko and M.M.Shcherbak [12] observed these same relationships in the case of 3-hydroxybenzaldehyde dissolved in alcohol with one mol of sodium alcoholate present. Here, too, a 10^{-4} molar solution yielded an absorption curve that nearly coincided with the curve for 3-hydroxybenzaldehyde in neutral alcohol. It is typical that in this instance 3-hydroxyacetophenone does not behave like 4-hydroxy, but rather like 2-hydroxyacetophenone, which also exhibits the phenomenon of alcoholysis and the restoration of its spectrum in a neutral solution at a concentration of 10^{-4} mol when its alcoholic solution containing one mol of sodium alcoholate is diluted. The salt that is formed is not alcoholized in the case of 4-hydroxyacetophenone [1].

The absorption curve of 3-hydroxyacetophenone dissolved in alcohol with 100 mols of sodium alcoholate present (Table 5 and Fig. 3, Curve 3) no longer exhibits the break in the absorption boundary as dilution is increased. At $\varepsilon =$ 100, the curve begins at $\lambda = 4070$ A, being the prolongation of the absorption curve 2 for a 10^{-2} molar solution containing one mol of sodium alcoholate. Rising steeply, the curve possesses a wide band (α_2) with a maximum at $\lambda = 3495$, $\varepsilon = 5000$. There is a bend in the curve at the shortwave edge of this band, between 3140 and 3260 A and $\varepsilon = 700$-1300. After dipping to a low minimum at $\lambda = 2940$ A and $\varepsilon = 100$, the curve displays two more bands: a narrow band (α_1) with a maximum at $\lambda = 2655$ A and $\varepsilon = 500$, and a very strong α_1' band with a maximum at $\lambda = 2380$ A and $\varepsilon = 30000$.

Table 6 lists the data on the band maxima of acetophenone in the presence of an excess of sodium alcoholate (after N.A.Valyashko and Yu.S.Rozum [10]), and of 3-hydroxy- and 3-methoxyacetophenone in neutral alcoholic solutions and in alcoholic solutions containing various amounts of sodium alcoholate.

Comparing the absorption curves of 3-hydroxyacetophenone in neutral alcohol and in alcohol with 100 mols of sodium alcoholate present (Curves 1 and 3, Fig. 3) shows that the presence of the alkali does not change the nature of the absorption curve in the neutral solution; the curve consists of the same three bands: α_2, α_1, and α_1'. The alkali causes: a) considerable shift of the whole absorption curve toward the longer wavelengths, the absorption being shifted most in the region of the longwave α_2 band, to wit: at $\varepsilon = 100$ and 560 A, the maximum being shifted 385 A, the shifts of the α_1 band and the α_1' band being much smaller (130 A and 200 A, respectively, while the minima are likewise shifted perceptibly toward the longer wavelengths (by 190 and 250 A, respectively); b) a perceptible decrease in the intensity of the α_1 band (by half) and of the absorption in the region of the minimum separating the α_2 and α_1 bands (to one-quarter). The drop in intensity and the large shift toward the longer wavelengths of the α_1' band, the α_1 band becomes less perceptible in an alkaline solution than in a neutral alcoholic solution.

We investigated 3-hydroxyacetophenone dissolved in alcohol with 1000 mols of sodium alcoholate present in solutions of the following concentrations: 10^{-3} to $2 \cdot 10^{-5}$ mol. The absorption curve (Table 5) begins at the same λ, as when 100 mols of sodium alcoholate are present, namely $\lambda = 4080$ A and $\varepsilon = 100$. Rising, the curve exhibits a band with a maximum at $\lambda = 3515$ A and $\varepsilon = 3500$; then it drops to a minimum at $\lambda = 2910$ A and $\varepsilon = 300$, rising again and exhibiting another, narrow, band with a maximum at $\lambda = 2360$ A and $\varepsilon = 23300$. This last band

TABLE 6

Compound	α_2 Band		φ Band		α_1 Band		α_1' Band	
	λ	ε	λ	ε	λ	ε	λ	ε
Acetophenone in alcohol with an excess of sodium alcoholate present	3210	50	2770	600	2420	10000	–	–
3-Hydroxyacetophenone in alcohol	3110	5000	Not manifested		2525	10000	2180	25000
3-Hydroxyacetophenone with 1 mol of sodium alcoholate	3105	5000	–	–	2530	10000	2190	26600
3-Hydroxyacetophenone with 100 mols of sodium alcoholate	3495	5000	–	–	2655	5000	2380	30000
3-Hydroxyacetophenone with 1000 mols of sodium alcoholate	3515	3500	–	–	Bend between 2760-2560 (3000-7000)		2360	23300
3-Methoxyacetophenone in alcohol ..	3085	3500	–	–	2490	7000	2185	16600
3-Methoxyacetophenone with 1000 mols of sodium alcoholate	3060	3000	–	–	2520	6000	–	–
3-Hydroxybenzaldehyde in alcohol ..	3180	3500	–	–	2550	10000	2200	20000
3-Hydroxybenzaldehyde with 220 mols of sodium alcoholate	3650	3000	–	–	2777	7000	2400	15000

is located in the same region of the spectrum as the band of 3-hydroxyacetophenone dissolved in alcohol to which 100 mols of sodium alcoholate have been added. The curve has a marked bend between 2760 and 2560 A and ε = 3000-7000. As we see in Fig. 3, the absorption curve of 3-hydroxyacetophenone with 1000 mols of sodium alcoholate present differs but little from the absorption curve of the same compound with 100 mols of sodium alcoholate; the longwave edges of their α_2 bands coincide, and the maxima in the α_2 and α_1' bands are only slightly shifted when 1000 mols of sodium alcoholate are present, their intensities being slightly less. As the concentration of alkali is increased, essential changes continue to occur only in the α_1 band, to wit: its intensity continues to drop, it appearing merely as a bend on the curve between 2760 and 2560 A. When 1000 mols of sodium alcoholate are present, the intensity likewise increases in the region of the minimum between the α_2 and α_1 bands. It is worthy of note that in alkaline solutions of 3-hydroxyacetophenone the absorption is increased in the region of the φ band of acetophenone, while the band λ = 2380 practically coincides with the position of the α_1 band of acetophenone (λ = 2420 A) in an excess of sodium alcoholate. Table 3 gives the data for the band maxima of 3-hydroxyacetophenone in alcohol and in alcohol with an excess of sodium alcoholate present, as reported by N.A.Valyashko and M.M.Shcherbak [12]. As these figures indicate, the effect of an excess of sodium alcoholate upon the absorption curve of 3-hydroxyacetophenone, to which reference has been made above, is the same as its influence upon the absorption of 3-hydroxybenzaldehyde. Apparently, the acetyl group causes only a somewhat smaller shift of the α_2 and α_1 bands toward the longer wavelengths than does the formyl group.

3-Methoxyacetophenone dissolved in alcohol with sodium alcoholate present. We investigated 3-methoxyacetophenone in alcoholic solutions whose concentrations ranged from 10^{-3} to 10^{-4} mol, with an excess of sodium alcoholate present – 1000 mols per mol of the substance. The absorption curve (Fig. 4, Curve 2) begins at ε = 100 and λ = 3430 A, rises steeply, and exhibits a band with a maximum at λ = 3060 A and ε = 3000; then the curve drops to a minimum at λ = 2735 A and ε = 400,

and, rising again, exhibits another band with a maximum at $\lambda = 2520$ A and $\varepsilon = 6000$. There is another minimum in the ultraviolet shortwave region at $\lambda = 2335$ A and $\varepsilon = 1000$. As we see from the absorption curves of 3-methoxyacetophenone in alcoholic solutions of sodium alcoholate (Fig. 4, Curves 1 and 2), as well as from the data in Table 3, the presence of an excess of alkali does not cause any essential change in the absorption curve of 3-methoxyacetophenone in neutral alcohol, as was the case with 3-hydroxyacetophenone. The curve consists of the same α_2 and α_1 bands, the positions of which are shifted ever so little (25 A toward the shorter wavelengths for the α_2 band, and 30 A toward the longer wavelengths for the α_1 band). Only the absorption intensity is noticeably reduced by the alkali in the region of the second minimum (by half).

Fig. 4. 1) 3-methoxyacetophenone, 10^{-3} to $5 \cdot 10^{-5}$ mol., in alcohol; 2) 3-methoxyacetophenone, 10^{-3} to 10^{-4} mol., in alcohol + 1000 mols. of C_2H_5ONa; 3) 3-methoxyacetophenone, 10^{-3} to $4 \cdot 10^{-5}$ mol., in alcohol + 4000 mols. of HCl.

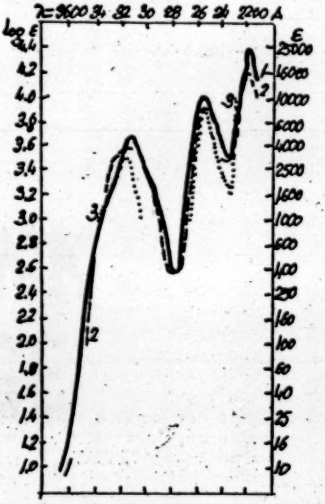


Fig. 5. 1) 3-Hydroxyacetophenone, 10^{-2} to $2 \cdot 10^{-5}$ mol, in alcohol; 2) 3-hydroxyacetophenone, 10^{-3} to $5 \cdot 10^{-5}$ mol., in alcohol + 4000 mols. of HCl; 3) 3-hydroxyacetophenone, 10^{-4} mol., in alcohol + 40,000 mols. of HCl.

3-Hydroxy- and 3-methoxyacetophenone in alcoholic solutions of HCl. We investigated 3-hydroxyacetophenone in alcoholic solutions of hydrogen chloride of the following concentrations: 10^{-3}, 10^{-4}, and $5 \cdot 10^{-5}$ mol with 4000 mols of HCl, and 10^{-4} mol with 40000 mols of HCl per mol of the substance. The absorption curve in an alcoholic solution with 4000 mols of HCl present coincides almost entirely with the curve for 3-hydroxyacetophenone in neutral alcohol, as we see in Fig. 5 (Curve 2) and in the data of Table 7, i.e., hydrogen chloride has no perceptible effect upon the absorption of 3-hydroxyacetophenone.

Nor does raising the concentration of HCl to 40000 mols per mol of the substance produce any substantial changes in the absorption curve of 3-hydroxyaceto-

TABLE 7

Compound	α_2 Band		α_1 Band		α_1' Band	
	λ	ε	λ	ε	λ	ε
3-Hydroxyacetophenone in alcohol	3110	5000	2525	10000	2180	25000
3-Hydroxyacetophenone in alcohol with 4000 mols of HCl	3145	4000	2525	9000	2185	17000
3-Hydroxyacetophenone in alcohol with 40000 mols of HCl	3155	3000	2515	9000	–	–
3-Methoxyacetophenone in alcohol	3085	3500	2490	7000	2185	16600
3-Methoxyacetophenone in alcohol with 4000 mols of HCl	[illegible]	3500	2500	8000	2195	22500

phenone in neutral alcohol. The only perceptible shift is that of the shortwave edge of the α_2 band (totaling 180 A at $\varepsilon = 1000$) toward the longer wavelengths, so that this band contracts; moreover, the intensity of the α_2 band and the absorption intensity in the region of the minimum between the α_1 and α_1' bands diminish, as has been found by N.A. Valyashko and M.M.Shcherbak [12] for 3-hydroxybenzaldehyde in alcoholic solutions of HCl as well.

We investigated 3-methoxyacetophenone in alcoholic solutions of hydrogen chloride at the following concentrations: 10^{-3}, 10^{-4}, and $4 \cdot 10^{-5}$ mol, with 4000 mols of HCl per mol of substance. The absorption curve (Fig. 4, Curve 3) is, by and large, unchanged by the presence of the HCl, as was the case with the 3-hydroxyacetophenone, and coincides with the curve for a neutral alcoholic solution. The only difference is a certain shift of the longwave edge and of the maximum of the α_2 band toward the shorter wavelengths, to the extent of 40 A (in 3-hydroxyacetophenone, on the other hand, this band maximum is shifted by the same 35-45 A, but toward the longer wavelengths, as compared with a neutral solution).

3-Hydroxyacetophenone in concentrated and dilute sulfuric acid. We investigated 10^{-3} molar and 10^{-4} molar solutions of 3-hydroxyacetophenone in concentrated (98%) sulfuric acid. The solution were an intense yellow. The absorption curve (Table 8, Fig. 6, Curve 2) begins at $\varepsilon = 100$ in the visible region of the spectrum, at $\lambda = 5000$ A, and rises slowly, exhibiting a clearly marked point of inflection at $\lambda = 4300$ A and $\varepsilon = 400$. After this inflection point, the curve rises more sharply, exhibiting a band with a maximum at $\lambda = 3720$ A and $\varepsilon = 5000$. The curve has two more bands, with maxima at $\lambda = 2935$ A and $\varepsilon = 13000$, and $\lambda = 2270$ A and $\varepsilon = 10000$. The minima that separate these bands are located at $\lambda = 3360$, 2465, and 2210 A and $\varepsilon = 2000$, 1000, and 4000, respectively.

Table 9 lists the data for the band maxima of 3-hydroxyacetophenone in alcohol and concentrated sulfuric acid; it also gives the data for the absorption of acetophenone in 96% sulfuric acid, as reported by Flexer, Hammet, and Dingwall [14] and by Bandow [15].

As we see from a comparison of the absorption curves of 3-hydroxyacetophenone in concentrated sulfuric acid and in alcohol (Fig. 6, Curves 1 and 2), as well as from the data in Table 9 , the presence of the acid produces substantial changes in the absorption, to wit: a) the absorption is sharply shifted toward the longer wavelengths; the beginning of absorption is shifted 1490 A at $\varepsilon = 100$ and 600 A at $\varepsilon = 1000$; the α_2 band of 3-hydroxyacetophenone in a neutral alcoholic solution is shifted by the presence of the acid nearly parallel toward the longer wavelengths (maximum shifted 610 A); the α_1' band, located at $\lambda = 2180$ A in alcohol, is likewise shifted by the acid toward the longer wavelengths, though less so

(maximum shifted 90 A), its intensity dropping considerably (by a factor of 2.5); b) the absorption in the region of the α_1 band, located at λ = 2525 A and ε = 10000, in neutral alcohol, is missing when sulfuric acid is present; instead, Curve 2 exhibits a pronounced minimum at λ = 2465 A and ε = 1000; c) the absorption is sharply increased in the 2900-3000 A region in concentrated sulfuric acid: a very strong band appears with a maximum at λ = 2935 A and ε = 13000; d) there is a point of inflection in the long wave region at $\lambda = \sim 4300$ A, when sulfuric acid is present, evidence of the presence of a band.

The absorption curve of 3-hydroxyacetophenone in the presence of concentrated sulfuric acid is rather much like that of unsubstituted acetophenone in 96% sulfuric acid (Curves 4 and 5). In both cases, we find a band with a maximum at λ = 2950 A, as shown in Fig. 6, together with a band in the longwave region of the spectrum; in both cases the α_1 band of these compounds is not present in alcohol or hexane. As Flexer, Hammet, and Dingwall [14], who investigated the absorption spectra of acetophenone in sulfuric acid solutions of various concentrations (from 50 to 95.99%), have discovered, the φ band of acetophenone, which is located at λ = 2800 A and ε = 1150 in an aqueous solution, is gradually shifted toward the longer wavelengths and becomes much stronger as the acid concentration is increased; as the acid concentration is increased, the α_1 band is also shifted toward the longer wavelengths, but its intensity, on the other hand, diminishes more and more, so that as it grown gradually fainter it merges with the φ band, the intensity of which rises pronouncedly. This apparently also is the case in 3-hydroxyacetophenone in concentrated sulfuric acid: the intensity of the α_1 band diminishes while the band itself falls into the area of the neighboring band, with a maximum at λ = 2935 A; the latter band resembles the φ band of unsubstituted acetophenone in concentrated sulfuric acid, merely somewhat lower in intensity. In other words, the presence of the acid promotes the growth of absorption in the φ band of acetophenone in both instances; the presence of a hydroxyl group in a meta position to the carbonyl group merely diminishes the intensity of the φ band somewhat. According to the authors cited, the α_2 band maximum of acetophenone, which is located at λ = 3325 A and ε = 50 in an aqueous solution, is not shifted toward the longer wavelengths as the concentration of sulfuric acid is increased; the maximum of this band is in fact 25 A farther over toward the shortwave region in 96% acid than in the aqueous solution; on the other hand, its intensity

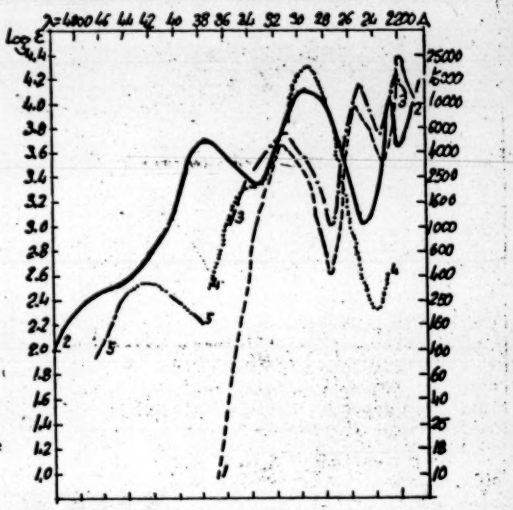


Fig. 6.

1) 3-Hydroxyacetophenone, 10^{-2} to $2 \cdot 10^{-5}$ mol., in alcohol; 2) 3-hydroxyacetophenone, 10^{-3} and 10^{-4} mol., in concentrated H_2SO_4; 3) 3-hydroxyacetophenone, 10^{-4} to 2.10^{-5} mol., in 10% H_2SO_4; 4) acetophenone in concentrated H_2SO_4; 5) the longwave band (ε reduced by a factor of 5) of acetophenone in concentrated H_2SO_4, according to Bandow.

rises perceptibly with the rise in the acid concentration, though not as much as in the case of the φ band. The intensity of this band also increases in solutions of alcoholic sulfuric acid. According to N.A.Valyashko and Yu.S.Rozum [10], who investigated the absorption of acetophenone in 63.85% alcoholic sulfuric acid, the α_2 band of acetophenone, which is located at $\lambda = 3210$ A and $\varepsilon = 50$ in neutral alcohol, grows much stronger when the acid is present, though, in contrast to what occurs in aqueous solutions, it is also noticeably shifted toward the longer wavelengths (by 90 A). In the case of 3-hydroxyacetophenone, the presence of acid has a somewhat different effect upon the α_2 band than in in acetophenone, namely: it is shifted considerably toward the longer wavelengths (the maximum being shifted by 610 A), while its intensity remains the same as in an alcoholic solution. Hence, whereas a hydroxyl group in the meta position to the carbonyl group merely reduces the intensity of the φ band, it increases the intensity of the α_2 band 100% over what we find in unsubstituted acetophenone, besides shifting it sharply toward the longer wavelengths. Here again we find our previous hypothesis confirmed: that the α_2 band of 3-hydroxyacetophenone, which is located at $\lambda = 3110$ A and $\varepsilon = 5000$ in alcohol, differs from the α_2 band of unsubstituted acetophenone, which has a maximum in alcohol at $\lambda = 3210$ A and $\varepsilon = 50$.

TABLE 8

3-Hydroxyacetophenone, 10^{-3} and 10^{-4} mol, in concentrated sulfuric acid		3-Methoxyacetophenone, 10^{-3} and 10^{-4} mol, in concentrated sulfuric acid		
λ	ε	λ		ε
5000	100	4900		100
4800	200	4300		600
4550	300	4200	bend	700
4300 bend	400	3800		2500
3800	4000	3725	maximum	3000
3720 maximum	5000	3650		2500
3640	4000	3350		1000
3440	2500	3300	minimum	900
3360 minimum	2000	3250		1000
3280	2500	3040		10000
3040	10000	2975	maximum	13000
2935 maximum	13000	2910		10000
2830	10000	2570		1300
2530	1300	2525	minimum	1200
2465 minimum	1000	2480		2000
2400	1300	2280		8000
2280	8000	2270	maximum	9000
2270 maximum	10000	2260		8000
2260	8000	2250		7000
2230	5000	2240	minimum	6000
2210 minimum	4000	2230		7000
2190	5000	2140		10000
2090	10000			

TABLE 9

Compound	α_2' Band		α_2 Band		φ Band		α_1 Band		α_1' Band	
	λ	ε	λ	ε	λ	ε	λ	ε	λ	ε
3-Hydroxyacetophenone in alcohol	–	–	3110	5000	–	–	2525	10000	2180	25000
3-Hydroxyacetophenone in a 10% aqueous solution of sulfuric acid	–	–	3095	6000	–	–	2505	15000	2195	17500
3-Hydroxyacetophenone in concentrated sulfuric acid	~4300	400	3720	5000	2935	13000	–	–	2270	10000
Acetophenone in concentrated sulfuric acid ..	~4200	2000	3300	2400	2950	20500	–	–	–	–

When concentrated sulfuric acid is present, 3-hydroxyacetophenone likewise has an absorption band at λ = 4300 A and ε = 400, over which the longwave edge of its α_2 band is superimposed, so that the band is manifested as merely a point of inflection. Bandow discovered a similar band, with a maximum at λ = 4200 A and ε = 2000, in acetophenone in concentrated sulfuric acid [15]. The cited influence of the acid grows much weaker as its concentration drops. Diluting a 10^{-3} molar solution of 3-hydroxyacetophenone in concentrated sulfuric acid with water to 10^{-4} mol decolorizes the solution completely. The absorption curve of such a solution (Fig. 6, Curve 3) starts at ε = 1000 and λ = 3540 A and, rising gradually, exhibits a wide α_2 band with a maximum at λ = 3095 A and ε = 6000; the curve then exhibits two more bands, with maxima at λ = 2505 A and ε = 15000 and λ = 2195 A and ε = 17500, respectively. Comparison of the absorption curves 2 and 3 in Fig. 6 indicates that this dilution results in eliminating the influence of the acid entirely. The curve is sharply shifted toward the shorter wavelengths, coinciding nearly completely with the curve for 3-hydroxyacetophenone dissolved in alcohol (Curve 1); compared to the latter, the sole changes are a slight rise in the intensity of the α_2' and α_1 bands and a drop in the intensity of the α_1' band, a widening of the α_2 band as the result of the rise in the absorption intensity in the minimum region, lying at λ = 2740 A, and a shift of the longwave edge of the α_2 band toward the longer wavelengths.

It follows from the foregoing that in dilute solution sulfuric acid acts, on the whole, like HCl, the sole difference being that in the former the α_2 band is wider, while in HCl the maximum of this band is shifted 50-60 A toward the longer wave lengths. The fact that diluting to 10^{-4} mol almost entirely restores the spectrum of 3-hydroxyacetophenone in alcohol or hexane indicates that the latter does not undergo any far-reaching chemical change in concentrated sulfuric acid.

3-Methoxyacetophenone in concentrated and dilute sulfuric acid. We investigated 10^{-3} and 10^{-4} molar solutions of 3-methoxyacetophenone in concentrated sulfuric acid. As was the case with 3-hydroxyacetophenone, the solutions were an intense yellow. The absorption curve begins at ε = 100 and λ = 4900 A (Table 8, and Fig. 7, Curve 2), and, rising upward, rounds off and at approximately 4200 A and $\varepsilon \sim$ 700, exhibits a clearly defined bend; then the curve rises, and exhibits a wide band with a maximum at λ = 3725 A and ε = 3000. After passing through a minimum at λ = 3300 A and ε = 900, the curve exhibits a strong band with a maximum at λ = 2975 A and ε = 13000. The curve has another, weaker, band at the shortwave end of the spectrum, with a maximum at λ = 2270 A and ε = 9000. The minimum spearating the two latter bands is located at λ = 2525 A and ε = 1000. The data on the band maxima of 3-hydroxy- and 3-methoxyacetophenone in concentrated sulfuric acid are listed in Table 10, together with the data on the absorption bands of the latter in alcohol. As we see from these figures and from a comparison of the absorption curves reproduced in Fig. 7, the presence of sulfuric acid produces the same changes in the absorption curve of 3-methoxyacetophenone as was the case in 3-hydroxyacetophenone. Compared to the alcoholic solution, the absorption is similarly shifted sharply toward the longer wavelengths, the same φ band and the band at $\sim$ 4200 A being manifested, as well as nearly the same intensity; the α_1 band is also absent, while the α_2 band is shifted toward the longer wavelengths by nearly the same amount as in the case of 3-hydroxyacetophenone, the strength of this band being the same as that in the alcoholic solution. As a result, the curves for 3-hydroxy- and 3-methoxyacetophenone nearly coincide in concentrated sulfuric acid, only minor differences existing, viz.: the start of absorption is shifted somewhat toward the shorter wavelengths in 3-methoxyacetophenone (by 100 A at ε = 100); at ε = 250 the 3-methoxy- curve intersects the 3-hydroxy- curve, after which it is shifted away from the latter toward the longer wavelengths (by 50 A at ε = 1000); and the minimum separating the α_2 and φ bands is much weaker in 3-methoxyacetophenone than

in 3-hydroxyacetophenone (half as strong) and is shifted 60 A toward the shorter wavelengths. On the other hand, the minimum lying between the φ and α_1' bands is shifted toward the longer wave lengths by the same 60 A in 3-methoxyacetophenone, its intensity remaining the same. The φ band maximum is likewise shifted toward the longer wavelengths in the 3-methoxy compound, by 40 A, while the intensity of the α_2 band is much weaker in 3-methoxythan in 3-hydroxyacetophenone, as was the case in the alcoholic solutions. It follows, therefore, that the influence of sulfuric acid upon absorption does not involve any reaction with the hydroxyl hydrogen, for this absorption influence is likewise observed in the methoxy compound.

In the case of 3-methoxyacetophenone again, diluting its 10^{-3} molar solution in concentrated sulfuric acid to form a 10^{-4} molar solution causes the cited influence of sulfuric acid to disappear. The absorption curve (Fig. 7, Curve 3) starts at ε = 1000 and λ = 3670 A, not coinciding with the end of absorption in the initial solution. The curve no longer has the bands that are characteristic of the solution in concentrated sulfuric acid, the curve resembling the one for the alcoholic solution completely. It consists of the same three bands as in alcohol or in hexane, the sole differences from the curve in alcohol involving a slight shift of the α_2 and α_1 bands toward the

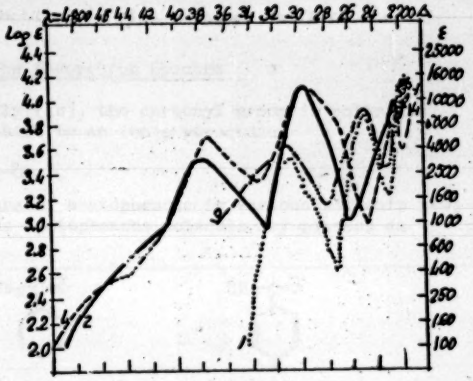


Fig. 7. 1) 3-Methoxyacetophenone, 10^{-3} to $5 \cdot 10^{-6}$ mol., in alcohol; 2) 3-methoxyacetophenone, 10^{-3} to 10^{-4} mol., in concentrated H_2SO_4; 3) 3-methoxyacetophenone, 10^{-3} to $2 \cdot 10^{-5}$ mol., in 10% H_2SO_4; 4) 3-hydroxyacetophenone, 10^{-3} and 10^{-4} mol., in concentrated H_2SO_4.

TABLE 10

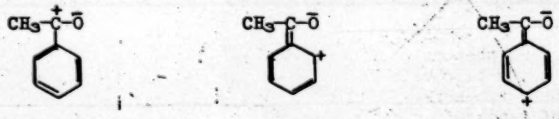
Compound	α_2^* Band		α_2 Band		φ Band		α_1 Band		α_1' Band	
	λ	ε	λ	ε	λ	ε	λ	ε	λ	ε
3-Methoxyacetophenone in alcohol	–	–	3085	3500	–	–	2490	7000	2185	16600
3-Methoxyacetophenone in a 10% aqueous solution of sulfuric acid	–	–	3110	4000	–	–	2510	8000	2160	16600
3-Methoxyacetophenone in concentrated sulfuric acid	~4200	700	3725	3000	2975	13000	–	–	2270	9000
3-Hydroxyacetophenone in concentrated sulfuric acid	~4300	400	3720	5000	2935	13000	–	–	2270	10000

longer wavelengths (25 and 20 A, respectively), with an equal shift of the α_1' band toward the shorter wavelengths.

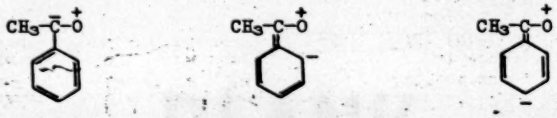
Evaluation of the Absorption Spectra

As has been pointed out repeatedly [16], the carbonyl group is polar in aldehydes and ketones, owing to its shift to an ionic structure:

Research on the absorption spectra of acetophenone in various solvents [10] has led to the view, however, that the acetophenone molecule may possess an oxonium structure:

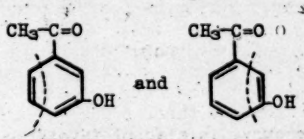


as well as a carbonium structure:



Apparently, acetophenone can exist in two states, formerly called the α- and φ states, with the α state containing carbonium structures and the φ state containing oxonium structures. This is in agreement with many other properties of acetophenone, especially with the meta and ortho orienting influence of the $COCH_3$ group [17]. The α state favors the development of the absorption in the α_2 and α_1 bands, yielding spectra of the α-type, while the φ state favors the development of absorption in the same region as in phenol, yielding spectra of the φ-type. The resemblance between the absorption spectra of acetophenone and benzaldehyde justifies the assumption that the latter may also exist in the α and φ states. Comparison of the absorption curves of benzaldehyde and of its hydroxy substitutes has shown [18] that the entrance of a hydroxyl group into the benzaldehyde ring at the ortho or meta position reinforces an absorption spectrum of the α-type; the entrance of the hydroxyl group at the para position leads to spectra of the φ-type. These conclusions were corroborated by researches on 2- and 4-hydroxyacetophenone [1]. Here, too, the ortho position favored the development of spectra of the α-type, while para-hydroxyl favored spectra of the φ-type. As we have seen above, an investigation of 3-hydroxy acetophenone favors the development of spectra of the α-type, as was the case in 3-hydroxybenzaldehyde.

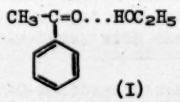
N.A.Valyashko [19] attributed this difference in the effect of the OH group to the nature of the conjugation of the carbonyl and hydroxyl groups with the benzene ring in the various isomers. When these groups enter into joint conjugation with the double bonds of the benzene ring, the development of a spectrum of the α-type is favored; individual conjugation of the OH group with the double bonds of the ring leads to the development of spectra of the φ-type. From this point of view, there are two different kinds of conjugation possible in 3-hydroxyacetophenone, as shown in the adjoining diagram.



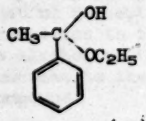
To judge by the nature of the absorption curve, the first type of conjugation predominates in the compound we have been investigating. But, as has been shown earlier, the absorption curve of 3-methoxyacetophenone also contains a band that coincides with the α_2 band in unsubstituted acetophenone. The band at = 2380 Å for 3-hydroxyacetophenone in an alkaline medium nearly coincides with the α_1 band in acetophenone. All this is evidence of the greater freedom of individual conjugation exhibited by the 3-hydroxy and 3-methoxyacetophenones in different media. The manifestation of spectra of the α-type in 3-hydroxy and 3-methoxyacetophenone may be explained by the fact that joint conjugation seems to promote an increase in the proportion of molecules with carbonium structures. The individual conjugation of the $COCH_3$ and OH or OCH_3 groups with the double bonds of the benzene ring ought to promote an increase in absorption in the bands that are typical of phenol or anisole (the φ band) and unsubstituted acetophenone.

In contrast to what is observed in 2-hydroxyacetophenone, which has an intramolecular hydrogen bond, the esterification of 3-hydroxyacetophenone does not affect the absorption curve in any significant manner. This is further confirmation of the resemblance between the optical effects of the OH and the OCH_3 groups, which has been found to exist in phenol and in anisole [20], and which is a result of the similar effect of these groups upon the benzene ring. In a solvent such as alcohol, the absorption curves of 3-hydroxy and 3-methoxyacetophenone are perceptibly shifted toward the longer wavelengths, though the spectrum is of the same α-type as that in hexane. This signifies that spectra of the α-type are developed still further in alcohol, evidently due to the effect of an intermolecular hydrogen bond. There is no reason to assume the existence of any appreciable intermolecular association in 3-hydroxyacetophenone in hexane at the concentrations we have investigated. The pattern is different in alcohol. Several investigations of infrared spectra have shown that the phenols display a strong band, characteristic of the OH group, when dissolved in neutral solvents (CCl_2, C_6H_6), due to the elimination of the association of phenol molecules in such solvents [21]. The band for the OH group vanishes altogether in solvents that can form hydrogen bonds, precisely because of the formation of hydrogen bridges with the molecules of the solvent [22].

The intramolecular hydrogen bond in 2-hydroxyacetophenone favors a greater shift of the α_2 and α_1 bands toward the longer wavelengths than is the case in 3-hydroxyacetophenone. The same effect is to be expected when intermolecular hydrogen bonds are established. The formation of associated coordination compounds of the type (I) promotes the shift of the carbonyl group to a carbonium structure, thus shifting absorption toward the longer wavelengths. A proportionate decrease in the intensity of the absorption bands is likewise observed when we change from hexane to alcohol as the solvent. This indicates that some of the molecules apparently weaken absorption in alcohol in the spectrum range under investigation. This may be due to the formation of a hemiacetal structure (II), as Herold has pointed out [23].



(I)



(II)

The presence of concentrated sulfuric acid causes a major change in the absorption curves of 3-hydroxy- as well as 3-methoxyacetophenone. This change involves a marked development of spectra of the α-type on the one hand, and of the spectra of the φ-type on the other. The principal reason for this, apparently, is the formation of an oxonium ion from the oxygen of the carbonyl group: $>C=\overset{+}{O}-H$, for these

changes in the spectrum occur in the unsubstituted acetophenone as well. The formation of such an ion when acetophenone or benzaldehyde are reacted with concentrated sulfuric acid has been established in the papers by Flexer, Hammet, and Dingwall [14], Baker [24], Kendall and Carpenter [25], Anderson [26], and others.

The addition of a proton to the carbonyl group ought to promote an appreciable increase in the number of molecules with a carbonium structure. This is in agreement with the increase in the meta-orienting action of the carbonyl group in concentrated sulfuric acid (Baker and Moffit [27]), as well as with the increase in the velocity of several reactions of ring-substituted acetophenones in an acid medium (Evans, Morgan, and Watson [28], etc.). The formation of an oxonium ion promotes the development of absorption in the α_2 band and the shift of that band toward the longer wavelengths. The increase in intensity is evidently related to the involvement of a larger number of the substance's molecules in absorption. The increase in the absorption intensity in the φ band region of acetophenone and its shift toward the longer wavelengths is apparently due to the pronounced increase in the polarization of the benzene ring's double bonds in the presence of sulfuric acid. In the hydroxy and methoxy-substituted acetophenones, this may be due to the polarizing effect of sulfuric acid upon the OH and OCH_3 groups. In his survey of weak bases, Hammet [29] concluded that there is no direct evidence that compounds containing a hydroxyl group act as bases in sulfuric acid. According to Kato and Someno [30], spectrographic analysis of phenol and anisole in sulfuric acid likewise indicates that the observed shift of the absorption curves of these compounds toward the longer wavelengths and the change in intensity may be due chiefly to the action of the strong poles of the sulfuric acid molecules upon the oxygen of the hydroxyl or methoxy group. This view is essentially the same as that of Baly and Rice [31] concerning the causes for the shift toward the longer wavelengths of the absorption curves of anisole, dimethylresorcinol, and other compounds in sulfuric acid.

SUMMARY

1. An investigation has been made of the absorption spectra in the ultraviolet of 3-hydroxy- and 3-methoxyacetophenone in hexane, alcohol, alcoholic solutions of sodium alcoholate and HCl, concentrated sulfuric acid, and aqueous solutions of sulfuric acid.

2. It has been found that the absorption spectra of 3-hydroxy- and 3-methoxyacetophenone are outgrowths of the absorption spectrum of unsubstituted acetophenone, as in the case of 2-hydroxyacetophenone and contrary to what was the case with 4-hydroxyacetophenone, they exhibit spectra of the α-type, with strong absorption in the α_2 and α_1 bands.

3. It has been found that the α_2 band of 3-hydroxy- and 3-methoxyacetophenone is a complex band, consisting of two superimposed bands: the α_2' and α_2'' bands, the first of which corresponds to the α_2 band of acetophenone.

4. It has been found that the absorption curve of 3-hydroxyacetophenone resembles that of 2-hydroxyacetophenone. The difference is that the α_2 band of 3-hydroxyacetophenone is shifted somewhat toward the shorter wavelengths and that no perceptible change occurs in the absorption curve as a result of the transition to the methyl ester of the 3-hydroxy compound. Changing from hexane to alcohol as the solvent causes the curve for 3-hydroxyacetophenone to be shifted somewhat to the longer wavelengths, in contrast to the curve for the 2-hydroxy compound.

5. Both 3-hydroxy- and 3-methoxyacetophenone retain their α-type spectra in all the media investigated. Only in concentrated sulfuric acid is there a

strongly developed spectra of the φ-type, alongside the α-type spectra.

6. It has been found that the curves for 3-hydroxy- and 3-methoxyacetophenone also contain bands that are characteristic of unsubstituted acetophenone and phenol. This is evidence of the greater freedom of individual conjugation of the $COCH_3$, OH, and OCH_3 groups in these compounds.

7. It has been shown that the foregoing peculiarities in the absorption of 3-hydroxy and 3-methoxyacetophenone may be explained on the basis of the assumption that these compounds may exist in two states: the α and the φ, the first state being characterized by joint, and the second by individual conjugation of their groups with the double bonds of the benzene ring.

LITERATURE CITED

[1] N.A.Valyashko and Yu.S.Rozum, J.Gen.Chem. 17, 755 (1947).
[2] R.Fuson, J.Am.Chem.Soc. 54, 1114 (1932).
[3] H.Rupe and K.Mayewski, Ber., 33, 3401 (1900).
[4] Bidginelli, Ber., 27, 580 (1894).
[5] P.Pfeiffer, Ann., 383, 141 (1911).
[6] E.Besthorn, E.Banshoff and G.Jaegle, Ber., 27, 3035 (1894).
[7] V.Meyer and P.Jacobson, Lehrbuch d. Org. Chem., B. II, 526 (1902).
[8] R.Auwers, Ann., 408, 246 (1925).
[9] T.Tasaki, Acta Phytochimica, 3, 259 (Chem. Zentr. 1927, II, 1945-1951).
[10] N.A.Valyashko and Yu.S.Rozum, J.Gen.Chem. 16, 593 (1946).
[11] H. Ley and Winghen, Ber., 67, 302 (1934).
[12] N.A.Valyashko and M.M.Shcherbak, J.Gen.Chem. 8, 1399 (1938).
[13] cf.: H. Ley, Handbuch d. Physik, 21, 484 (1929).
[14] L.Flexer, L.Hammet, and A.Dingwall, J.Am.Chem.Soc., 57, 2103 (1935).
[15] F.Bandow, Biochem. Z., 296, 81 (1938).
[16] L.Pauling, Prog.Chem., 7, 9 (1938); C. Ingold, Chem. Rev., 15, 225 (1934); B. Eistert. Tautomerie und Mesomerie (1938).
[17] R.Camps, Arch. d. Pharm., 240, 1 (1902).
[18] N.A.Valyashko, J.Russ.Chem.Soc. 42, 751 (1910).
[19] N.A.Valyashko, J.Russ.Chem.Soc., 58, 779 (1926).
[20] M.Horio, J.Soc.Chem.Ind. Jap., 37, 284 (1934).
[21] R.Freyman, Comptes rend., 204, 41 (1937).
[22] W.Gordy and L.Nielsen, J.Chem.Phys., 6, 12 (1938) and others.
[23] W.Herold, Z. phys. Chem, B 18, 265 (1932).
[24] Baker, J.Chem.Soc., 1931, 307.
[25] I.Kendall and C.Carpenter, J.Am.Chem.Soc., 36, 2498, (1914).
[26] L.Anderson and C.Googing, J.Am.Chem.Soc., 57, 999 (1935).
[27] Baker and Moffit, J.Chem.Soc., 1931, 314.
[28] D. Evans, V.Morgan, and H.Watson, J.Chem.Soc., 1935, 1167.
[29] L.Hammet, Chem. Rev., 13, 61 (1933).
[30] S.Kato and F.Someno, Chem. Zentr., 1938, II, 3909.
[31] E.Baly and F.Rice, J.Chem.Soc., 1912, 1475.

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THE SAPONIN OF THE ROOTS OF PATRINIA INTERMEDIA R. ET SCHULT

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Patrinia intermedia R. et Schult, fam. Valerianaceae, is a perennial with an extensive root system that abounds in the foothills of the Zailiisky Ala-tau.

We have found that the roots of patrinia contain 13% of saponin (Korsakova's method). Analysis of the root ashes indicated that the latter contain an appreciable quantity (17-22%) of calcium and potassium oxides. The method of extracting saponin with water was therefore useless, inasmuch as heating with water might result in alkaline hydrolysis of the saponin molecule; fungi appear when the water processing is slow. Nor could the baryta method [1,2] be employed since the saponin secured was physiologically inactive. We therefore extracted the saponin from the roots of patrinia by the alcoholic method, percolation with 80% alcohol [2,3].

The crude saponin was a strong adhesive (glued various objects), hygroscopic, brown mass, that contained 1.6% of ash. The mineral substances were eliminated from the saponin by reprecipitating it repeatedly with ether from 80% alcohol.

The doubly reprecipitated saponin had an ash content of 0.62%. Somewhat better results were secured by reprecipitating the saponin by ether from 96% alcohol (3:1), but even this did not reduce the ash content below 0.6%. It should be noted that other authors have also commented on the high ash content of the saponins [1]. The pure (triply recrystallized) saponin was dried in a 15-mm vacuum at 100° for 5 hours above $CaCl_2$. The melting point (decomposition) of the saponin was 180°.

The saponin was freely soluble in water, methanol, ethyl alcohol, acetic acid, pyridine, and weak alkalies and acids (better when heated). It is practically insoluble in petroleum ether, gasoline, benzene, chloroform, acetone, dichloroethane, carbon tetrachloride, carbon disulfide, n-butyl and isoamyl alcohols, ethyl acetate, or sulfuric ether; nor is it soluble in dilute phenol, naphthalene, or concentrated acids and alkalies. When aqueous solutions of the saponin are shaken they form large amounts of a stable foam. The foaming value at 26° was 13.

A 1% solution in alcohol had a $[\alpha]_D^{16.2}$ of -0.42°. The surface tension of a 1% aqueous solution was 61.46 dynes/cm. The viscosity of a 1% aqueous solution at 25° was 9.14 centipoises. The molecular weight of the saponin, dried for 5 hours above P_2O_5, in a 15 mm vacuum at 100°, was 964 (cryoscopic method – water as the solvent).

Analysis of the saponin indicates that its formula is $C_{53}H_{88}O_{15}$.

Found %: C 64.47, 65.12; H 8.33, 9.04. Computed %: C 65.97; H 9.12.

The saponin forms precipitates with barium hydroxide and lead salts (sugar of lead as well as vinegar of lead). The saponin does not contain a carboxyl group. The pH of an aqueous solution of the saponin is 3.86.

The saponin is precipitated by tanic acid; only a few saponins (guaiac-saponins) exhibit this reaction. The saponin of patrinia possesses reducing properties: it reduces silver from an ammoniacal solution, it converts mercuric chloride into calomel, and it reduces permanganate.

The saponin does not reduce Fehling's solution in the cold or when cautiously heated, merely turning it green. The saponin exhibits several color reactions that are typical of the saponins: the reaction with concentrated H_2SO_4, the Liebermann reaction, and the Levine reaction.

The chemical properties of the saponin lie midway between the so-called "neutral" saponins and the "saponic acids". The isolated saponin forms a binary compound with cholesterol – a so-called saponin cholesteride. (We know that only those saponins form saponin cholesterides that belong to the group of sterols.)

The patrinia saponin is hydrolyzed fairly easily by mineral acids. When the saponin is hydrolyzed by 5% hydrochloric acid, the hydrolyzate is strongly colored. Clarifying the hydrolyzate with activated charcoal results in the loss of the carbohydrate component, totaling 16.7% by weight of the saponin. The best conditions for hydrolysis are heating the saponin with 5% H_2SO_4 for 5 hours with a reflux condenser over a water bath. The yield of sapogenin totals 64.1% and that of the reducing substances 33.6% by weight of the saponin.

The saponin molecule has been found to contain fructose (17.43% by weight of the saponin), identified as its p-nitrophenylhydrazone (m.p. 179-181°) and by the Selivanov reaction. No other hexoses were found. A total of 14.68% of pentose (by weight of the saponin) was found by the phloroglucide method.

We believe that saponin is hydrolyzed as follows:

$$\underset{\text{saponin}}{C_{53}H_{88}O_{15}} \longrightarrow \underset{\text{sapogenin}}{2C_{21}H_{32}O_2} + \underset{\text{fructose}}{C_6H_{12}O_6} + \underset{\text{pentose}}{C_5H_{10}O_5}. \qquad (I)$$

The subjoined table lists the yields called for by this equation alongside the actual yields of the hydrolysis products.

Hydrolysis products	Per cent yield	
	According to Equation (I)	Actual
Sapogenin	65.83	64.13
Fructose	18.43	17.43
Pentose	15.62	14.68

We propose to call the saponin extracted from the roots of patrinia patrinin.

Patrinin is extremely toxic in tadpoles. The latter die within 16 hours after having been placed in a 1:120,000 aqueous solution of the saponin. Patrinin hemolyzes blood, i.e., its action is like that of snake poisons. Our data, not reproduced here, indicate that the purer the patrinin, the weaker its hemolytic action. The saponin prepared by the baryta method did not hemolyze blood. The hemolytic index of pure patrinin with respect to horse's blood is 1:40,000.

The hemolysis of defibrinated blood caused by a solution of the saponin may be stopped by cholesterol (1 g of cholesterol to 5 g of the saponin).

We likewise tested the action of a 0.1% aqueous solution of the saponin on brewer's yeast. Fermentation set in and ended faster in test tubes containing

a solution of the saponin that had previously been irradiated for 10 minutes with ultraviolet light.

Isolation of the saponin. 200 g of the dried, finely ground roots was treated with three liters of 80% alcohol, using 200 ml at a time. The processing of 18 kg yielded 24.2 liters of a transparent dark-red extract. During the course of 6 days a flocculent, mucilaginous precipitate settled out, which was not investigated. After the alcohol had been driven off and the extract had been evaporated over a water bath, we secured a sticky, dark-brown mass that could be drawn out into threads. Reprecipitation with ether from 80% alcohol and drying in vacuum yielded 1.15 kg of the saponin as an amorphous light-brown powder, with an ash content of 0.62%.

Purifying the saponin. The saponin was dissolved by cautiously heating it in 96% alcohol, and three volumes of ether were added to the resulting solution at 20°. The addition of the first few batches of ether caused the solution to grow turbid, subsequent additions causing the deposition of a precipitate as individual threads, which subsequently condensed together, forming a loose, bulky mass. The ether solution was decanted, and the precipitate was immediately dried in vacuum. (The precipitate was transferred quickly, inasmuch as the mass darkens rapidly upon exposure to the air.) We found that all the water was eliminated from the saponin by drying it at 100° over $CaCl_2$ in a 15 mm vacuum, so that there was no need to desiccate it above P_2O_5.

Synthesis of the saponin cholestride. 1 ml of a 1% alcoholic solution of cholesterol was added to 1 ml of a boiling 1% alcoholic solution of the saponin, and the mixture was allowed to stand at room temperature for 2 days; beautiful transparent red crystals settled out in the shape of platelets piled on top of one another.

SUMMARY

1. A saponin totaling 13% by weight of the roots has been isolated from the roots of Patrinia intermedia R. et Schult, family Valerianaceae.

2. The molecular formula of the saponin has been found to be $C_{53}H_{88}O_{15}$.

3. The saponin is hydrolyzed as follows:

$$\underset{\text{saponin}}{C_{53}H_{88}O_{15}} \longrightarrow \underset{\text{sapogenin}}{2C_{12}H_{32}O_2} + \underset{\text{fructose}}{C_6H_{12}O_6} + \underset{\text{pentose}}{C_5H_{10}O_5}.$$

4. The saponin isolated is physiologically active and is a steroid saponin.

LITERATURE CITED

[1] R.Kobert. Die Saponine. Abderhalden's biochemisches Handlexikon, 7, 145 (1910).

[2] L.Kofler. Saponine. Klein's Handbuch der Pflanzenanalyse, 3, 1095 (1932).

[3] R.Kobert. Darstellung der Saponine. Abderhalden's Handbuch der biochemischen Arbeitsmethoden, 2, 790 (1910).

THE SAPOGENIN OF THE ROOTS OF PATRINIA INTERMEDIA R. ET SCHULT

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The sapogenins are the principal products of the hydrolytic cleavage of the saponins. The percentage of sapogenin usually ranges from 20.4 (in aegiceras saponin [1]) to 65.8 (hedaragenin from α-hederine [2]). The sapogenins are usually refined by repeated reprecipitation from alcohol or chromatographically.

Most of the pure sapogenins are crystalline substances, mostly white in color (though light-yellow ones are also encountered: melanthigenin [5] and Sapindus sapogenin), the amorphous ones being less common (Assam sapogenin [3], strophantigenin [2], macleaytin [5], and cyclameritin).

In contrast to the saponins, the sapogenins are not very hygroscopic (the exceptions being saponalbin and Randia sapogenin).

The sapogenins also differ from their saponins in possessing sharp melting points, which are higher than the melting points of the saponins, usually ranging from 250 to 350°. In contrast to the saponins, sapogenins are usually biologically inactive [6], which is probably due to the fact that they are practically insoluble in water. The sapogenins are very sparingly soluble in gasoline, benzene, toluene, chloroform, or ether. They are more soluble than the saponins in other solvents, with the exception of water. The sapogenins are very soluble in ethyl alcohol, methanol, acetic acid, and especially in pyridine. A characteristic of the sapogenins is their containing hydroxyl groups, ranging from one in oleanolic acid [7] to three in agavogenin [8]. Hence, the formation of acetyl (benzoyl) and methyl derivatives is typical of the sapogenins. Some sapogenins contain a carbonyl group, such as botogenin, cryptogenin, cammogenin [8], etc.

At the present time all the sapogenins are divided into two large classes: the steroids and the triterpenoids.

The underlying structure of steroid sapogenins is the ring system of reduced cyclopentenophenanthrene, with methyl groups attached to the C_{10} and C_{13} atoms and with a hydroxyl group attached to the C_3 atom [10, 11].

The underlying structure of triterpenoid sapogenins consists of the ring system of picene. Moreover, the triterpenoid sapogenins, in contrast to the steroid sapogenins, possess a carboxyl group.

The steroid sapogenins are likewise distinguished by the formation of a binary compound with a cholesteride, whereas the triterpenoid sapogenins do not form such compounds. The side chain of the steroid sapogenins is a spiroketoacetal [12].

What is highly characteristic of the steroid sapogenins is their conversion into physiologically active substances of the sex hormone type [13]. Recent researches [14] have demonstrated that sarsasapogenin and diosgenin are practical sources of supply for the production of such sex hormones as progesterone (the

female sex hormone) and testosterone (the male sex hormone) [15].

We have reported that the hydrolysis of a saponin (patrinin) with 5% H_2SO_4 resulted in a sapogenin yield that totaled 64.19% by weight of the saponin. The sapogenin, recrystallized five times from 96% alcohol, was a white substance containing no ash (elongated white needles under the microscope). After having been dried at 100° above $CaCl_2$ in a 15-mm vacuum, the sapogenin contained neither water of crystallization nor alcohol. It turns concentrated H_2SO_4 orange-red.

When cautiously heated to 250-258° in a drying cabinet, the sapogenin sublimed, forming elongated, light, white fibers with a m.p. of 265.5°.

The sapogenin does not affect cold-blooded animals; it does not irritate the mucous membranes of the eyes or the nose, nor does it affect the skin. It is insoluble in water or concentrated acids and alkalies; it is sparingly soluble in petroleum ether, gasoline, benzene, xylene, toluene, ethyl acetate, acetone, dichloroethane, carbon tetrachloride, isoamyl alcohol, n-propyl alcohol, absolute ethyl alcohol, dilute phenol, and naphthalene. It is freely soluble in 80% alcohol and in 96% alcohol (when heated); it is very soluble in acetic acid (60%, 80%, and glacial), methanol, and particularly in pyridine.

The molecular weight of the sapogenin, desiccated above P_2O_5 at 100° for 5 hours 15 mm, was determined cryoscopically (glacial CH_3COOH as the solvent); it was 316. Analysis of the sapogenin yielded the formula $C_{21}H_{32}O_2$.

Found %: C 78.71, 78.80; H 10.19, 10.47. $C_{21}H_{32}O_2$. Computed %: C 79.74; H 10.12.

The absence of any hydroxyl groups was established by acetylating and methylating it. The absence of any carbon-carbon double bond was established by means of a qualitative reaction for an unsaturated bond and by catalytic hydrogenation (above Ni in alcohol). Titrating the sapogenin with an alcoholic alkali [16] proved that it had no carboxy, aldehydic, or ether groups. A qualitative Legall reaction [4] was negative (absence of a lactone ring). We synthesized: the dioxime of the sapogenin as an amorphous substance with a m.p. of 203-205°; the monosemicarbazone, an amorphous substance with a m.p. of 196-199°; and the bis-2,4-dinitrophenylhydrazone with a m.p. of 248-251° (with decomposition). Oxidation of the sapogenin with chromic anhydride at 60° yielded the substance $C_{18}H_{28}O_6$ with a m.p. of 247-250° (decomposition) and isovaleric acid. Oxidation with permanganate in a neutral medium yielded a substance with a m.p. of 173-174° (% C = 44.22; % H = 8.28), which was not investigated further.

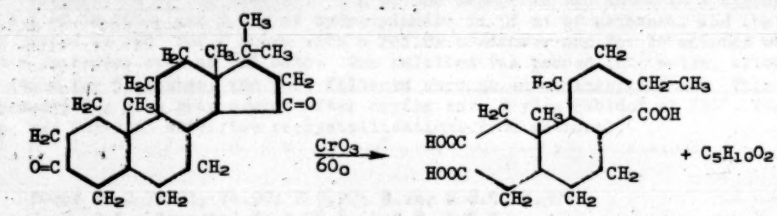
The absence of a carboxyl group in the sapogenin and the formation of a saponin cholesteride indicate that the sapogenin is a steroid. The synthesis of derivatives that are characteristic of the diketones is evidence of the presence of two keto groups in the sapogenin, one of them being less reactive than the other. This explains the synthesis of a monosemicarbazone instead of the di- derivative, as well as the not very smooth reaction involved in the formation of the bis-2,4-dinitrophenylhydrazone. Inasmuch as the hydroxyl group is always attached to the C_3 atom in steroid sapogenins, it is quite possible that one of the keto groups in the sapogenin derived from patrinin is at the same position. The second keto group is probably attached to the C_{15} atom, since isovaleric acid was formed during the oxidation of the sapogenin. This arrangement of the groups resembles that of the hydroxyl groups (at C_3 and C_{15}) in digitogenin [2]. The hydroxyl group at C_{15} in digitogenin is less reactive than the other such groups, attached to the C_2 and C_3 atoms.

The patrinin sapogenin also differs from other steroid sapogenins in the structure of its side chain, which consists of 2 carbon atoms (the side chains

of other steroid sapogenins always consisting of 8 carbon atoms).

We believe that the chromic-acid oxidation of the patrinin sapogenin involves the rupture of the carbon-carbon bond of the sterol ring that usually occurs in sterols and steroids at the place where the hydroxyl (in our case the keto) groups are attached to the C_3 and C_{15} atoms, forming carboxyl groups.

The structural formula of the sapogenin we have isolated and its oxidation by chromic acid may be represented as follows:



The ring rupture we have observed also occurs in estrone [4].

We propose to call the sapogenin prepared from the patrinin of the roots of Patrinia intermedia R. et Schult patringenin. It is quite possible that patringenin, as a steroid sapogenin, may be a source of supply for synthesizing compounds related to the sex hormones.

EXPERIMENTAL

Recovery and refining of the sapogenin. 87.3 g of the pure saponin (patrinin) was placed in a flask (capacity 5 liters), and 2 liters of 5% H_2SO_4 was poured over it. The resulting opaque, dark-brown solution was heated for 9 hours with a reflux condenser over a water bath. A bulky light-brown precipitate was observed after 2 hours of heating. The formation of a precipitate ceased after 5 hours of continuous hydrolysis. The precipitate was filtered out on an ordinary filter and carefully washed (until the SO_4" reaction disappeared). The sapogenin precipitate was a light-yellow mass, resembling moist clay. The yield of the crude sapogenin totaled 56.04 g, i.e., 64.19% by weight of the saponin.

Recrystallization from 96% alcohol yielded the sapogenin as a voluminous, caseous, grayish mass. A constant melting point was attained after five recrystallizations from 96% alcohol. The yield of the pure sapogenin totaled 17.63 g, or 20% by weight of the saponin.

Acetylation. 2 g of the sapogenin was mixed with 0.5 g of CH_3COONa, and 20 ml of acetic anhydride was added to the mixture. The mixture was then heated over a water bath with a reflux condenser for 3 hours, transferred to a porcelain dish after it had cooled to room temperature, and treated with 25 ml of water with constant stirring. The resultant precipitate was filtered out and recrystallized from 80% alcohol; after it had been dried in vacuum it was a white substance with a m.p. of 265°, i.e., the sapogenin was recovered unchanged.

Methylation with diazomethane. 1 g of the sapogenin was suspended in 5 ml of anhydrous ether, and diazomethane was passed through the suspension for 25 minutes at 0° and for 5 minutes at room temperature. The solution was then covered and allowed to stand for 3 days. The ether was evaporated in air, and the deposit was recrystallized from 80% alcohol; this yielded the sapogenin unchanged (m.p. 265°).

Preparation of the bis-2,4-dinitrophenylhydrazone. 1 g of 2,4-dinitrophenylhydrazine dissolved in 25 ml of 96% alcohol containing 1 ml of concentrated HCl was added to a hot solution of 1 g of the sapogenin in 25 ml of 96% alcohol. A flocculent yellow precipitate settled out after 10 minutes of standing. A brownish-red precipitate settled out after 36 hours under the same conditions. Both precipitates were subjected to fractional crystallization from alcohol. The dark-red precipitate has a m.p. of 248-251° (with decomposition) after recrystallization from alcohol and drying in vacuum.

Preparation of the dioxime. 1 g of the sapogenin was added to a mixture of 1 g of CH_3COONa and 0.8 g of hydroxylamine in 50 ml of methanol, and the whole was heated to 140° for 4 hours with a reflux condenser and for 10 minutes without a condenser over an oil bath. The solution was poured into water, allowed to stand for 5 minutes, and then filtered through an ordinary filter. This yielded 370 g of a gray powder after drying in a drying cabinet at 120°. Its m.p. was 203-205° after two recrystallizations from methanol.

Found %: C 75.01, 74.90; H 9.22, 9.24; N 8.5, 8.37.
$C_{21}H_{34}O_2N_2$. Computed %: C 72.8; H 9.8; N 8.9.

Preparation of the semicarbazone. 0.5 g of the sapogenin was dissolved in 25 ml of alcohol, and 25 ml of pyridine and 0.5 g of semicarbazide hydrochloride was added to the resulting alcoholic solution. The mixture was heated over a water bath for 10 minutes to speed up dissolution of the semicarbazide. The transparent gold-colored solution was allowed to stand for 7 days at room temperature. Thirty minutes after 30 ml of water was added to the solution a fine-grained gray precipitate settled out of the solution; it was washed with cold water, dried in a drying cabinet at 120°, recrystallized from 96% alcohol, and dried in vacuum, after which its m.p. was 196-198.5°; the yield was 180 mg.

Found %: C 70.70, 70.74; H 9.40, 9.43; N 11.29, 12.
$C_{22}H_{35}O_2N_3$. Computed %: C 70.77; H 9.37; N 11.92.

Oxidation of the sapogenin with chromic anhydride. 5 g of the sapogenin was placed in 300 ml of glacial CH_3COOH and heated to 60° over a water bath; then 4 g of chromic anhydride dissolved in 50 ml of 80% CH_3COOH was gradually added from a buret, with constant stirring. It took 3 hours for the oxidizing agent to be added.

After the mixture had cooled to room temperature, 50 ml of water was added, with 25 mol of ether added 20 minutes after that. The ether processing of the mixture was repeated three times with batches of 25 ml each, the solution being vigorously shaken after each batch had been added. After the ether solution had been separated, it was washed three times with 25 ml batches of water and three times with 3% NaOH.

During the washing the ether solution separated into three layers: an ether layer, an alkaline layer, and between them, a middle layer consisting of a greenish, slightly cloudy liquid. The middle layer was removed, and the ether and alkaline layers were processed together.

After the ether had been driven off from the combined ether and alkaline layers and the remainder had been treated with 10 ml of 10% H_2SO_4, a white precipitate settled out; it was washed with dilute H_2SO_4 and recrystallized from ether. The slightly grayish powder fused at 247-250°; the yield was 0.68 g.

Found %: C 60.16; H 7.45. $C_{18}H_{28}O_8$. Computed %: C 61.12; H 8.27.

The middle layer was evaporated to a syrupy state over a water bath and then processed with 0.5 ml of water. 25 ml of copper acetate was added to the

resulting emulsion, and the mixture was heated for 20 minutes. After the mixture had stood for 30 minutes, a precipitate settled out, which was treated three times with 0.5 ml of water. The combined filtrate and wash waters (1 ml) were separated into two parts. One part was gently heated with 0.25 ml of 5% $ZnCl_2$ for 30 minutes. The precipitate was filtered out and dissolved in 0.5 ml of water, and the solution was slowly evaporated in the open air. The small amount of grayish residue was identified as the zinc salt of isovaleric acid (the form and arrangement of the crystals were the same as those of zinc isovalerate [2]). The other half of the filtrate was processed with 0.5 ml of 80% CH_3COOH, and 0.5 ml of acetone was added to the solution. The precipitated CH_3COONa was filtered out, and 0.5 ml of a 5% solution of $Cu(CH_3COO)_2$ and 5 drops of dilute alcohol were added to the filtrate, collected on watch glass. Slow evaporation in the open air resulted in the settling of a green precipitate. The product was microphotographically identified as the copper salt of isovaleric acid [17].

SUMMARY

1. Hydrolysis of a saponin (patrinin) with 5% H_2SO_4 yielded a sapogenin (patringenin), amounting to 64.19% by weight of the saponin. The yield of the pure sapogenin totaled 20.26%.

2. The molecular formula of the sapogenin was found to be $C_{21}H_{32}O_2$.

3. The following derivatives of the sapogenin have been prepared: the bis-2,4-dinitrophenylhydrazone, the semicarbazone, and the dioxime.

4. Oxidizing the sapogenin with chromic anhydride yielded isovaleric acid and the acid $C_{16}H_{28}O_8$.

5. A structural formula is proposed for the sapogenin.

LITERATURE CITED

[1] C. Wehmer, W.Thies, and M. Hadders. C. Klein's Handbuch der Pflanzenanalyse, I, 856 (1932).
[2] L.Kofler, Saponine, Loc. cit., 3, 1095 (1932).
[3] Van Rijn, Die Glykoside, S. 175, Berlin (1900).
[4] L. Fieser. The Chemistry of Phenanthrene Derivatives (Russ. Ed.), 475. State Chemical Press (1941).
[5] R.Kobert, Die Saponine. E.Abderhalden's Biochemisches Handlexikon, 7 145 (1910).
[6] E.Sieburg. Isolierung, Nachweis und Abbaustudien auf dem Gebiete der Saponine, E. Abderhalden's Handbuch d. biol. Arbeitsmethoden, Berlin, 544 (1923).
[7] H.Grosshof and E.Wedekind, Ber., 60, 2686 (1936).
[8] R.E.Marker, R.Wagner, P.Ulshafer, E.Wittbecker, D.Goldsmith and C. Rouf, J.Am.Chem.Soc., 69, 2167 (1947).
[9] R.E.Marker and J Lopez, J.Am.Chem.Soc., 69, 2397 (1947).
[10] R.E.Marker and E.Rohrmann, J.Am.Chem.Soc., 61 1291 (1939).
[11] R.E.Marker, T.Tuskamoto, and D.Turner, J.Am.Chem.Soc., 62, 2525 (1940).
[12] Marker, Wagner, and others, J.Am.Chem.Soc., 65, 499 (1943).
[13] L.Fieser and R.Jacobsen, J.Am.Chem.Soc., 60, 28 (1938).
[14] R.E.Marker and E.Rohrmann, J.Am.Chem.Soc., 62, 518 (1940).
[15] R.E.Marker, J.Am.Chem.Soc., 62, 2543 (1940).
[16] H.Meyer. Analysis and Determination of the Structure or Organic Substances (Russ. ed.) 424. United Scientific and Technical Press (1935).
[17] J.Schmidt. Die organische Saüre. C. Klein's Handbuch d. Pflanzenanalyse, 1, 386, 401 (1932).

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THE ALKALOIDS OF DELPHINIUM OREOPHILUM III

ALKALOIDS OF THE FAMILY RANUNCULACEAE. V

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In 1941 one of the present authors (S.Y.) observed extensive fields of blue Delphinium in the Shakhristan Pass through the Turkestan range. An expedition of our institute (headed by E.E.Korotkov), working in this region in the summer of 1947, brought back a large quantity of this plant, which was identified as Delphinium oreophilum Huth. Preliminary investigations of the plant indicated a high alkaloid content, which led us to make a more detailed study of it.

As the name indicates (oreophilum = mountain-loving), Delphinium oreophilum is a plant confined to high altitudes. It is found in patches at 3200-3600 meters, where the air is very thin, and the plant's period of bloom often coincides with the early mountain snowfalls. As in all the species of Delphinium we have investigated, the alkaloid content, in terms of percentage by weight of the dried plant, varies widely with the season. The behavior pattern established previously [1] holds good here, too, namely, that the alkaloids move to the green portions of the plant during the period of sprouting and bloom, while they pass into the seed, for the most part, after flowering is past and as the end of the vegetation season approaches, passing into the bark and roots, as well, in the perennials. The D. oreophilum collected in July, for example, at the very beginning of the flowering period, contained 0.95% of alkaloids in the green parts of the plant and 1.07% in the roots. The percentage of alkaloids in the above-ground organs of the plant, collected in the same area in August, when the fruit was ripening, dropped to 0.58%, while the percentage in the roots rose to 1.65%.

The customary dichloroethane extraction and subsequent alkalinization of the acid extracts with ammonia yielded an amorphous powder, which was precipitated as a thick, finely crystalline paste when its alcoholic solution was diluted with water. The crystals were filtered out and dried; all their properties proved to be the same as those of the alkaloid delsemine, recently isolated by us from D. semibarbatum [2]. The melting point of a mixed test sample bore out their complete identity. Heating the alkaloid with an alcoholic solution of caustic potash yielded the amino alcohol delsine and delseminic acid, which were also fully the same as the compounds described previously:

$$C_{37}H_{53}O_{10}N_3 + H_2O = C_{25}H_{41}O_7N + C_{12}H_{14}O_4N_2.$$

The discovery of a new, rich source of delsemine enabled us to make a more detailed study of the products of its hydrolytic cleavage and to establish the nature of delseminic acid. When delsemine is heated in 10% hydrochloric acid, the alkaloid is split into three products,- ammonia, a basic substance, and an acid:

$$C_{37}H_{53}O_{10}N_3 + 2H_2O = C_{32}H_{48}O_8N_2 + C_5H_8O_4 + NH_3.$$

The dibasic acid $C_5H_8O_4$ was readily identified as l-methylsuccinic acid.

The basic substance turned out to be anthranoyldelsine, as was proved by the alkaline hydrolysis of the base:

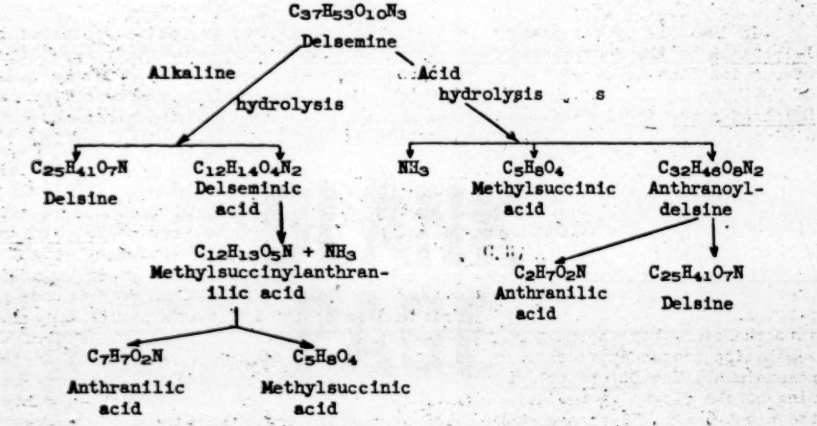
$$C_{32}H_{46}O_8N_2 + H_2O = C_{25}H_{41}O_7N + C_7H_7O_2N.$$

A parallel set of tests of delseminic acid yielded similar results. Heating delseminic acid with lime evolved ammonia and yielded the dibasic acid $C_{12}H_{13}O_5N$. When the latter was saponified in acid solutions, it was split into anthranilic and methylsuccinic acids, so that it must be the anthranilide of methylsuccinic acid:

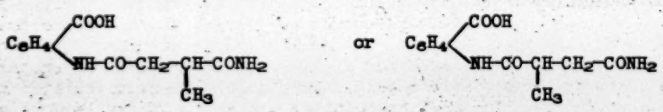
$$C_{12}H_{14}O_4N_2 + H_2O = C_{12}H_{13}O_5N + NH_3;$$

$$C_{12}H_{13}O_5N + H_2O = C_7H_7O_2N + C_5H_8O_4.$$

The overall picture of the hydrolytic cleavage of delsemine may be presented as follows:

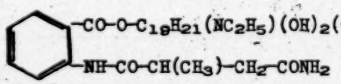


Hence, delseminic acid is amidomethylsuccinylanthranilic acid, and the only two possible formulas for it are:



Apparently, the position of the methyl group can only be determined by synthesis.

The partially expanded formula for delsemin ought to look like this:



In our previous report we pointed out that delseminic acid can exist in two forms with different melting points, and suggested that one of these was a racemic form. A more detailed study of the properties of delseminic acid and of

its saponification product, methylsuccinylanthranilic acid, has shown, however, that both of these acids may exist in two forms, irrespective of their optical properties, changing from one form into the other under suitable circumstances. This may well be an instance of amido-imido tautomerism:

Amidic form — Iminohydrin form

Less likely, though not impossible, is a syn- and anti-imino isomerism:

Orlov pointed out the existence of such a tautomerism and isomerism as far back as 1905 for the anilide and toluides of formic acid [3]. In any event, the reversibility of both of these forms is definitely proved by the fact that both of the isomers of delseminic acid yield the same optically active l-methylanthranilic acid upon hydrolysis.

	Anthranoyl-delsine	Anthranoyllycoctonine		
	Our data	Schulze and Bierling [4]	Goodson [5]	Marion and Edwards [6]
Melting point	166°*	154-155°	172°*	Amorphous
$[\alpha]_D$ in alcohol	+ 49.2°	–	–	+ 54°
$[\alpha]_D$ in HCl	+ 27.5°	–	+ 32.4°	+ 24°
Perchlorate (melting point)	216°	Begins to decompose at 185°	–	207°*

As has been pointed out already [2], some of the properties of the amino alcohol delsine resemble those of the alkaloid lycoctonine, which has been isolated by various authors from different species of Aconitum and Delphinium. Inasmuch as the physicochemical constants given for lycoctonine by different research workers differ greatly, it was of some interest to compare the corresponding figures for the anthranoyl esters of lycococtonine and delsine.

We see from the table that the properties of the anthranoyl ester of our alkaloid are as different from those of anthranoyllycococtonine as was the case for delsine itself.

EXPERIMENTAL

Isolation and purification of the alkaloids. The quantitative determination and recovery of the alkaloids were effected by methods similar to those employed for D. semibarbatum, the only difference being that the comparative purity of the extracted bases enabled us to simplify some of the operations somewhat. 12.0 kg of the dried and pulverized roots of the July harvest were wetted with 12 liters of a 5% solution of ammonia and allowed to stand for 2-2.5 hours, after which they were flooded with dichloroethane. The extraction should be done in a room with as low a temperature as is feasible. Every day the dichloroethane

*Corrected melting points.

extract was poured off and shaken with sulfuric acid: 20% acid being used at first, followed by two shakings with 5% acid. The resulting emulsion was eliminated by suction filtering. The acid solutions were combined, shaken with ether to eliminate any traces of dichloroethane, filtered out, and alkalinized while strongly chilled by gaseous ammonia drawn from a tank. The precipitated crude delsemine was suction-filtered out and desiccated in vacuum with calcium chloride. Weight: 115.0 g. The aqueous mother liquor, which totaled 6.5 liters was exhaustively extracted with chloroform. The dark, thick mass left after the chloroform had been driven off (13.4 g) was a mixture of delsemine and delsine. The total yield of the alkaloids was 128.4 g (1.07% of the dry weight of the roots).

To refine it, the crude delsemine was dissolved in 150 ml of alcohol. The alcoholic solution was filtered, and then diluted with an equal volume of water, considerable cloudiness being produced. The turbidity was dissolved by heating the mixture over a water bath, and the solution was slowly chilled after having been seeded with a few crystals of delsemin from D. semibarbatum. The next day the whole container was filled with a solid crystalline mass of delsemine. Triple recrystallization from dilute alcohol yielded a wholly pure, colorless base. The yield of the pure product totaled 60.2 g. The delsemine of D. oreophilum had a m.p. of 121-124° after having been dried in vacuum, and it exhibited no depression when mixed with the delsemine of D. semibarbatum. $[\alpha]_D^{22}$ + 44.2° (l = 2.2 in alcohol). 3.0 g of the base was dissolved in alcohol and heated with 4.3 ml of 1 N caustic potash. All the physicochemical constants of the delsine and delseminic acid produced by this saponification were the same as those of the compounds recovered from D. semibarbatum.

Acid hydrolysis of delsemine. 4.5 g of the base was heated for an hour over a water bath with 45 ml of a 10% solution of hydrochloric acid. The cooled solution was extracted 12 times with equal volumes of ether. After the methylsuccinic acid had been filtered out, the solution was alkalinized in the cold with 65 ml of a 10% solution of caustic potash, an excess of the alkali being avoided. The precipitated crude anthranoyldelsine was suction filtered out, washed twice with water, and dried in the air. Weight: 3.2 g. The wash waters were combined with the bulk of the filtrate, and the latter was extracted repeatedly with ether. Evaporating the ether extract yielded another 0.4 g of anthranoyldelsine. The aqueous solution from which the base had been isolated was realkalinized and warmed, and the ammonia driven off was collected in a flask containing a solution of hydrochloric acid. Neutralizing the ammonia consumed 28.8 ml of 0.2 N HCl. The calculated figure for one equivalent is 31.7 ml.

Anthranoyldelsine. The base, which settled out of alcohol as nearly colorless regular prisms, fused with turbidity at 166° after double recrystallization (it contracts at 158°). Further recrystallization did not affect the melting point of the alkaloid. Solutions of the base exhibited beautiful violet fluorescence. Anthranoyldelsine is very slightly soluble in water or petroleum ether, and slightly soluble in ether or benzene. Its solubility in alcohol depends largely upon what contaminations it contains – pure anthranoyldelsine is slightly soluble in cold alcohol (1:100).

0.2844 g substance in 25.0 ml of an alcoholic solution; l 10.0; α_D + 0.56°, $[\alpha]_D^{30}$ + 49.2°. 0.2200 g substance in 11.0 ml of 0.18 N solution of HCl; l 10.0; α_D + 0.55°, $[\alpha]_D^{32}$ + 27.5°.

0.1020 g substance: 0.2440 g CO_2; 0.0730 g H_2O. 0.1142 g substance: 0.2738 g CO_2; 0.0826 g H_2O. 0.1077 g substance: 5.0 ml N_2 (27°, 722 mm). 0.1080 g substance: 5.2 ml N_2 (26.5°, 722 mm). 0.0281 g substance: 11.29 ml 0.1 N $Na_2S_2O_3$. Found %: C 65.28, 65.43; H 8.01, 8.09; N 4.83, 5.02;

OCH_3 20.77. $C_{32}H_{46}O_8N_2$. Computed %: C 65.50; H 7.90; N 4.77; 4 OCH_3 21.22.

Anthranoyldelsine perchlorate. 0.5 g of anthranoyldelsine was dissolved in 8 ml of 1 N HCl and mixed with 2 ml of a saturated solution of ammonium perchlorate. A thick oil settled out at once, gradually solidifying. Minute lustrous needles simultaneously made their appearance in the mother liquor. When recrystallized from alcohol, the anthranoyldelsine perchlorate settled out as barely yellowish, lustrous, rectangular prisms, which fused at 216° with decomposition. Recrystallization did not change the melting point of the salt. Anthranoyldelsine perchlorate is slightly soluble in cold alcohol or water. Its solutions display violet fluorescence.

0.2490 g substance in 10.0 ml alcohol: l 10.0; α_D + 0.71°, $[\alpha]_D^{31}$ + 28.5°. 0.1040 g substance: 0.0204 g AgCl. 0.1112 g substance: 0.0224 g AgCl. Found %: Cl 4.85, 4.98. $C_{32}H_{46}O_8N_2 \cdot HClO_4$. Computed %: Cl 5.16.

When anthranoyldelsine was decomposed with ammonia, the crystalline anthranoyldelsine was precipitated unchanged. Marion and Edwards [8], whose physicochemical constants for anthranoyllycoctonine monoperchlorate are fairly close to our values, secured only a tarry base during this process. In general, it must be said that the crystallizability of our base is much higher than that of their salt.

l-Methylsuccinic acid. Evaporation of the ether extract of an acid secured during the hydrochloric hydrolysis of delsemine left behind a light-yellow oil, which gradually crystallized. Yield: 0.71 g. The crystals sticking to the oil were dissolved in 4 ml of water. The small quantity of anthranilic acid was filtered out of the aqueous solution, which was then evaporated to dryness in the open air. The l-methylsuccinic acid fused at 109-110° after recrystallization from a benzene-ether mixture.

0.2012 g substance in 10.0 ml water; l 10.0; α_D -0.15°; $[\alpha]_D^{24}$ -7.5°. 0.1044 g substance: 0.1728 g CO_2; 0.0592 g H_2O. 0.0960 g substance: 0.1590 g CO_2; 0.0552 g H_2O. 0.0610 g substance: 9.38 ml 0.1 N KOH (against phenolphthalein). Found %: C 45.17, 45.20; H 6.34, 6.43; equiv. 65.0. $C_5H_8O_4$. Computed %: C 45.45; H 6.10; equiv. 66.0.

The small quantity of acid was racemized by boiling it with caustic potash. The racemic methylsuccinic acid melted at 112°. It exhibited no depression when mixed with synthetic methylsuccinic acid.

Hydrolysis of anthranoyldelsine. 4.5 ml of a 1 N solution of caustic potash was added to a hot solution of 2.5 g of the base in 25 ml of methanol, and the alcohol was driven off rapidly. The residue was diluted with 20 ml of water, causing the instantaneous precipitation of crystalline delsine with a m.p. of 139°. The crystals (1.2 g) were filtered out and washed, and the combined filtrate was exhaustively extracted with chloroform; driving off the latter yielded another 0.4 g of delsine. The alkaline solution was acidulated with hydrochloric acid and extracted eight times with equal volumes of ether. The 0.5 g of crystals secured by evaporating the ether fused at 146° after recrystallization from hot water and exhibited no depression when mixed with anthranilic acid.

α- and β-Delseminic acids. α-Delseminic acid, which was described in our last report, was synthesized by precipitating the acid with strong inorganic acids from a solution of its salts. The acid settled out as light-yellow nodules when recrystallized from dilute alcoholic solutions by water or ether, the nodules clustering into large warty aggregates; m.p. 170-171°. When the α-acid is heated for a long time and then recrystallized from hot water, it changes into the β form, with a m.p. of 180-181°. This latter acid crystallizes as extremely small colorless needles. It can be reconverted into the α-form by re-

reprecipitating it from alkaline solutions. The β-form is unstable, turning into a form with a m.p. of 176° when stored for a long time. We did not investigate the nature of the latter in any detail. Both the α- and the β-form of the acid yield the same l-methylsuccinic acid when hydrolyzed.

Saponification of delseminic acid. A mixture of 2.0 g of the acid and 2.0 g of lime was boiled with 40 ml of water until no more ammonia was evolved. The cooled suspension was dissolved by adding 10% hydrochloric acid, and the solution was repeatedly extracted with ether. The thick mass left after the ether had been driven off was dissolved in 16.0 ml of 1 N caustic potash. The methylsuccinylanthranilic acid was precipitated from the solution of its salt by fractional neutralization: it was first converted into its monopotassium salt by adding 8 ml of 1 N hydrochloric acid and filtered through charcoal, then half of the acid, still rather dirty, was precipitated by adding another 4 ml of HCl, and, finally, the addition of the last 4 ml of HCl, a drop at a time, yielded all the acid, almost pure. The yield totaled 1.2 g.

α- and β-methylsuccinylanthranilic acid. The technical acid was purified by repeated fractional salting out from solutions of its salts. Recrystallization by this method yielded the α-acid with a m.p. of 166° (contracts at 163-164°). The β-form of the acid melts at 171°. The conversions of one form into the other take place under the same conditions as obtain for delseminic acid. Goodson [5] gives a m.p. of 155° and $[\alpha]_D^{24}$ -7.0° for l-methylsuccinylanthranilic acid. We isolated an optically inactive acid. Methylsuccinylanthranilic acid is readily soluble in alcohol (better than delseminic acid), slightly soluble in cold water or ether.

0.1034 g substance: 0.2166 g CO_2; 0.0490 g H_2O. 0.0986 g substance: 0.2068 g CO_2; 0.0472 g H_2O. 0.1126 g substance: 6.4 ml N_2 (29.5°, 719 mm). 0.1046 g substance: 5.6 ml N_2 (23°, 727 mm). 0.0776 g substance: 6.30 ml 0.1 N KOH (against phenolphthalein). Found %: C 57.17, 57.25; H 5.30, 5.36; N 5.81, 5.73; equiv. 123.2. $C_{12}H_{13}O_5N$. Computed %: C 57.36; H 5.22; N 5.58; equiv. 125.6.

Hydrolysis of methylsuccinylanthranilic acid. 0.8 g of methylsuccinyl acid was heated over a water bath with 10 ml of 10% HCl for 1.5 hours. The initially undissolved acid entered solution as it was saponified. When the reaction was over, the mixture was cooled and filtered. The hydrochloric acid was extracted with ether 14 times. The ether extract, which displayed light blue fluorescence, was evaporated to dryness. The residue was diluted with water and left to stand overnight. The crystals that had settled out by the next morning (0.36 g) were filtered out, dried, and identified as anthranilic acid. The aqueous mother liquor was extracted with ether; concentrating the ether extract yielded 0.34 g of methylsuccinic acid.

SUMMARY

1. The alkaloids delsemine and delsine, previously found by the authors in Delphinium semibarbatum, have been isolated from Delphinium oreophilum. The alkaloid content of the plant fluctuates widely with the period of growth.

2. The new products of the hydrolytic cleavage of delsemine: anthranoyldelsine, $C_{32}H_{46}O_8N$, and methylsuccinylanthranilic acid, $C_{12}H_{13}O_5N$, have been investigated.

3. The nature of delseminic acid has been ascertained; it turns out to be l-amidomethylsuccinylanthranilic acid.

4. α- and β-isomeric forms of delseminic and methylsuccinylanthranilic acids have been found.

LITERATURE CITED

[1] S.Yunusov, Bull. Uzbek Acad. Sci., 1948, 4, 11

[2] S.Yunusov and N.K.Abubakirov, J.Gen.Chem. 21, 174 (1951).*

[3] E.Orlov, J.Russ.Chem.Soc. 37, 439-442 (1905).

[4] H.Schulz and E.Bierling, Arch. der Pharm., 251, 8 (1913).

[5] J.A.Goodson, J.Chem.Soc. 1943, 139.

[6] L.Marion and O.E.Edwards, J.Am.Chem.Soc. 69, 2010 (1947).

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*See CB translation p. 189 ff.

XXXIII. THE ACTIVITY OF AMINES IN THE TRANSFORMATION OF HETEROCYCLIC COMPOUNDS CONTAINING OXYGEN INTO COMPOUNDS CONTAINING NITROGEN

Yu. K. Yuriev and I. K. Korobitsyna

In one of our previous reports we showed that N-phenylpyrrole or N-phenylpyrrolidine is produced by the reaction of furan or furanidine, respectively, with aniline at 400° in the presence of alumina, practically no pyrrole or pyrrolidine, respectively, being formed [1].

The present paper deals with the comparative activity of aliphatic amines and aniline, as well as with the action of corresponding mixture upon the reaction of secondary aliphatic-aromatic amines with furanidine.

It has been found that nothing but N-phenylpyrrolidine is produced when furanidine is reacted with mixtures of ethylamine and aniline, propylamine and aniline, butylamine and aniline, and cyclohexylamine and aniline; the N-alkyl pyrrolidines are either not produced at all or are formed in negligible quantities (N-ethylpyrrolidine, for example, could be identified only as its picrate).

The reaction of furanidine with secondary aliphatic-aromatic amines – ethylaniline, propylaniline, butylaniline, and cyclohexylaniline – likewise results in the formation of N-phenylpyrrolidine, together with unsaturated hydrocarbons: ethylene, propylene, butylene (butene-1), and cyclohexene, respectively.

The results secured in the present research are listed in the subjoined table.

The data in the table indicate that the reaction of furanidine with mixtures of aliphatic amines and aniline, as well as with mixtures of aniline with aliphatic-aromatic amines, yields analogous results, both in respect of the course of the reaction (formation of N-phenylpyrrolidine) and of the yields of the reaction products. The reactions are selective, insofar as the formation of N-phenylpyrrolidine is concerned:

$$+ C_nH_{2n} + H_2O + NH_3$$

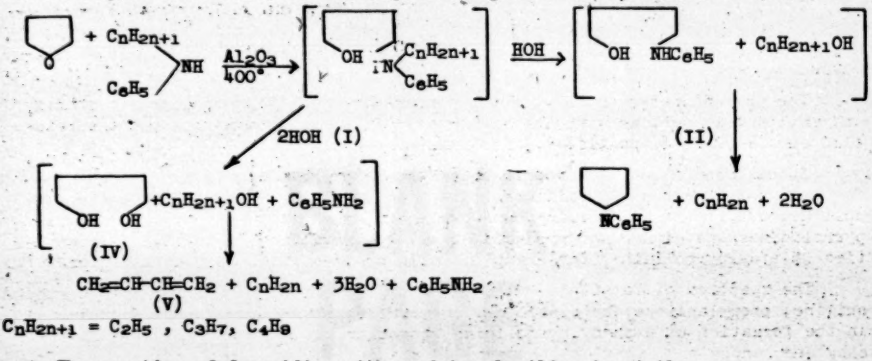
$C_nH_{2n+1} = C_2H_5$, C_3H_7, C_4H_9.

This equation also holds good for the reaction of furanidine with a mixture of aniline and cyclohexylamine, which yields N-phenylpyrrolidine and cyclohexene.

The explanation for such selectivity is the same as in the reaction of furanidine with an ammonia-aniline mixture [1]: aniline is a weaker base than the aliphatic amines. The ionization constants are: $K_pH = 4.58$ for aniline, $K_pH = 10.68$ for ethylamine, $K_pH = 10.58$ for propylamine, $K_pH = 10.61$ for butylamine,

and KpH = 10.64 for cyclohexylamine [2], so that the rupture of the carbon-oxygen polar bond in furanidine (the dipole moment of furanidine in benzene at 25° = 1.71 D [3]) occurs more readily when the furanidine reacts with aniline than with the aliphatic amines.

When furanidine is reacted with secondary aliphatic-aromatic amines, the 4-alkylphenylamino-1-hydroxybutane (I) [4] formed as an intermediate product is hydrolyzed by the water in the alumina, the high strength of the bond between the amino nitrogen and the phenyl radical causing the aliphatic radical to split off, yielding a saturated alcohol to begin with and forming a second intermediate reaction product – 4-phenylamino-1-hydroxybutane (II). The latter is then dehydrated, yielding an unsaturated hydrocarbon and N-phenylpyrrolidine (III). The 4-alkylphenylamino-1-hydroxybutane (I) was also hydrolyzed at both of its N-C (alkyl) bonds; this occurred in every instance, as is indicated by the formation of 1,3-butadiene (V) as the dehydration product of 1,4-butandiol (IV):



C_nH_{2n+1} = C_2H_5 , C_3H_7, C_4H_9

The reaction of furanidine with cyclohexylaniline is similar.

EXPERIMENTAL

1. Reaction of furanidine with ethylamine and aniline. A reaction mixture consisting of 10 g of furanidine, 12 g of aniline, and 6 g of ethylamine (1:1:1 molar proportions) was passed at a rate of 6-8 drops per minute in a current of nitrogen through a tube filled with alumina and heated to 400°. The catalyzate was collected in a receiver chilled with a snow-and-salt mixture. The run was repeated twice, using the same quantities each time.

The ether was driven out of the ether extracts of the catalyzate after the latter had been desiccated with potassium hydroxide; distillation of the residue yielded 0.5 g of a fraction that distilled at 102-110° (745 mm) and had a n_D^{20} 1.4490. The picrate produced by mixing the ether solutions of this fraction with picric acid fused at 185-186° after recrystallization from alcohol, and, hence, was the picrate of N-ethylpyrrolidine.

Literature data: b.p. 103.5-104.5° (747 mm) [5,6]; n_D^{20} 1.4352; d_4^{20} 0.8156; m.p. of picrate 186°; b.p. 104.5-105.5° (755 mm); n_D^{20} 1.4336; d_4^{20} 0.8084; m.p. of picrate 185-186° [4].

The catalyzate residue (constituting the bulk of the latter after the N-ethylpyrrolidine fraction had been isolated) was double-distilled in vacuum. Distillation yielded 18 g of aniline (75% of the quantity placed in the reaction), b.p. 74-75° (12 mm), n_D^{20} 1.5860, and 7 g of N-phenylpyrrolidine (16.5% of the

theoretical, based on the furanidine placed in the reaction, and 73.5% of the theoretical, based on the reacted aniline).

B.p. 105-106° (5 mm); n_D^{20} 1.5850; d_4^{20} 1.018; MR_D 48.39; Computed for $C_{10}H_{13}NF_3$ 46.51; EM_D 1.88.

Literature data: B.p. 114° (9 mm); n_D^{20} 1.5853; d_4^{20} 1.0183; EM_D 1.86; picrate m.p. 116° [4]

Thus, reacting furanidine with an aniline-ethylamine mixture yields N-phenylpyrrolidine plus traces of N-ethylpyrrolidine.

2. Reaction of furanidine with ethylaniline. A reaction mixture consisting of 9 g of furanidine and 15 g of ethylaniline (1:1 molar ratio) was passed over alumina at 400° in a current of nitrogen at the rate of 6-8 drops per minute. Two wash bottles containing bromine were connected to the receiver, which was chilled with snow and salt.

The customary processing of the catalyzate yielded the following reaction products: 6.5 g of aniline (55% of the theoretical), b.p. 63-65° (8 mm); n_D^{20} 1.5798; acetanilide m.p. 114°; and 2 g of N-phenylpyrrolidine (11% of the theoretical, based on the furanidine placed in the reaction, and 25% of the theoretical based on the reacted ethylaniline.

B.p. 115-117° at 10 mm; n_D^{20} 1.5820; d_4^{20} 1.0156; MR_D 48.37; computed for $C_{10}H_{13}NF_3$ 46.51; EM_D 1.86.

The contents of the bromine bottles were washed with a 10% solution of caustic soda and then with water, and desiccated with calcium chloride. Fractional distillation yielded 13.2 g of ethylene bromide (60% of the theoretical), the constants of which were as follows:

B.p. 130-132° (757 mm); n_D^{20} 1.5370; d_4^{20} 2.1753; MR_D 26.98; computed for $C_2H_4Br_2$ 26.96.

Literature data: B.p. 129.5° (745 mm); d_4^{20} 2.1785 [6]; d_4^{20} 2.1816; n_D^{20} 1.5379 [7]; n_D^{13} 1.5404 [8].

The residue left after the ethylene bromide had been driven off crystallized; it fused at 117-118° after recrystallization from petroleum ether. It was 1,2,3,4-tetrabromobutane. A test sample exhibited no depression when mixed with pure 1,2,3,4-tetrabromobutane.

Literature data: m.p. 116-119° [9]; m.p. 116-117° [10].

Thus, reacting furanidine with ethylaniline yields N-phenylpyrrolidine, ethylene, and a small amount of divinyl.

3. Reaction of furanidine with a propylamine-aniline mixture. A reaction mixture consisting of 5 g of furanidine, 4 g of propylamine, and 6.5 g of aniline (1:1:1 molar proportions) was passed over alumina at 400°. The customary processing of the catalyzate yielded: 3.8 g of aniline (58.5% of the quantity used for the reaction), b.p. 53-56° (3 mm); n_D^{20} 1.5801; and 1 g of N-phenylpyrrolidine (10% of the theoretical, based on the furanidine placed in the reaction, and 23.5% of the theoretical, based on the reacted aniline):

B.p. 102-104° (3 mm); n_D^{20} 1.5810; d_4^{20} 1.023; MR_D 47.83; computed for $C_{10}H_{14}NF_3$ 46.51. EM_D 1.32.

Thus, reacting furanidine with a propylamine-aniline mixture yields N-phenylpyrrolidine, no N-propylpyrrolidine being formed at all.

4. Reaction of fruanidine with propylaniline. A reaction mixture consisting of 9 g of tetrahydrofuran and 17 g of propylaniline (1:1 molar ratio) was passed

Reaction of Furanidine with Mixtures of Aliphatic Amines and Aniline, and with Secondary Amines with the same Radicals

(at 400° above Alumina)

Test No.	Original substances		Molar proportions	Reaction products						Remarks
				Tertiary amines			Unsaturated hydrocarbons or their dibromides			
	Heterocyclic compounds containing oxygen	Amines		Name	% yield (based on furanidine	% yield (based on the reacted aniline)	Name	% yield	% yield aniline	
1	Furanidine	Aniline and ethylamine	1:1:1	N-phenylpyrrolidine N-ethylpyrrolidine	16.5 Traces	73.5	-	-	75	-
2	"	Ethylaniline	1:1	N-phenylpyrrolidine	11	25	1,2-Dibromoethane	60	55	Some 1,2,3,4-tetrabromobutane
3	"	Propylamine and aniline	1:1:1	"	10	23.5	-	-	58.5	-
4	"	Propylaniline	1:1	"	8.5	16.5	1,2-Dibromopropane	78	50	Some 1,2,3,4-tetrabromobutane
5	"	Butylamine and aniline	1:1:1	"	4	9	-	-	54.5	-
6	"	Butylaniline	1:1	"	13	30	1,2-Dibromobutane	66	57	Some 1,2,3,4-tetrabromobutane
7a	"	Cyclohexylamine and aniline	2:1:1	"	4	9.5	Cyclohexene	60.5	60	-
7b	"	Cyclohexylamine and aniline	1:1:1	"	6	14.5	"	67	62.5	-
8	"	Cyclohexylaniline	1:1	"	6	13.5	"	60	59	-

over alumina at 400° at the rate of 6-8 drops per minute. The receiver, chilled with snow and salt, was connected to two wash bottles containing bromine. The customary processing of the catalyzate yielded the following reaction products: 6 g of aniline (50% of the theoretical), b.p. 63-66° at 8 mm, acetanilide m.p. 113.5°; and 1.7 g of N-phenylpyrrolidine (8.5% of the theoretical, based on the furanidine placed in the reaction, and 18.5% of the theoretical, based on the reacted propylaniline):

B.p. 111-113° (8 mm); n_D^{20} 1.5818; picrate m.p. 115-116°.

The bromination product yielded 19.5 g of 1,2-dibromopropane (78% of the theoretical):*

B.p. 139-141° (758 mm); n_D^{20} 1.5196; d_4^{20} 1.9347; MR_D 31.71; computed for $C_3H_6Br_2$ 31.58.

Literature data: b.p. 141.5-141.9° (corr.); d_4^{18} 1.9307 [11] d_4^{20} 1.9333 [12]; b.p. 140-141° [13].

The residue left after the 1,2-dibromopropane had been driven off yielded 1,2,3,4-tetrabromobutane, with a m.p. of 116.5°.

Thus, reacting furanidine with propylaniline yields N-phenylpyrrolidine, propylene, and a small amount of divinyl.

5. Reaction of furanidine with a butylamine-aniline mixture. A reaction mixture consisting of 8 g of furanidine, 9 g of butylamine, and 11 g of aniline (1:1:1 molar proportions) was passed over alumina at 400° in a current of nitrogen. The ether extracts of the catalyzate were desiccated, and the ether was driven off, yielding the following reaction products: 6.1 g of aniline (54.5% of the amount used for the reaction) with a b.p. of 75-77° at 13 mm, n_D^{20} 1.5800; acetanilide with m.p. 113-114°; and 0.7 g of N-phenylpyrrolidine (4% of the theoretical, based on the furanidine placed in the reaction, and 9% of the theoretical, based on the reacted aniline):

B.p. 110-111° (8 mm); n_D^{20} 1.5835; d_4^{20} 1.0221; MR_D 48.18; computed for $C_{10}H_{13}N$, 46.51; EM_D 1.67.

Thus, reacting furanidine with a butylamine-aniline mixture yields N-phenylpyrrolidine, no N-butylpyrrolidine being formed at all.

6. Reaction of furanidine with butylaniline. A mixture of 13.5 g of butylaniline and 6.5 g of furanidine (1:1 molar ratio) was passed over alumina at 400°. The gaseous reaction products were absorbed in bromine. The customary processing of the catalyzate yielded the following reaction products: 4.8 g of aniline (57% of the theoretical) with a b.p. of 58-60° at 4 mm, acetanilide m.p. 113°; and 1.7 g of N-phenylpyrrolidine (13% of the theoretical, based on the furanidine placed in the reaction, and 30% of the theoretical, based on the reacted butylaniline):

B.p. 113-114° at 9 mm; n_D^{20} 1.5840; d_4^{20} 1.0200; MR_D 48.31; computed for $C_{10}H_{13}N$ 46.51; EM_D 1.80. 5.200 mg substance: 0.448 ml N_2 (27°, 751 mm). 2.235 mg substance; 0.199 ml N_2 (26°, 753 mm). Found %: N 9.69, 9.81. $C_{10}H_{13}N$. Computed %: N 9.52.

The bromination product yielded 13.1 g of 1,2-dibromobutane (66% of the theoretical).

B.p. 165-166° (750 mm); n_D^{20} 1.5160; d_4^{20} 1.8132; MR_D 35.95; computed for $C_4H_8Br_2$ 36.20.

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*The yield of 1,2-dibromopropane was somewhat higher than that of the ethylene bromide or 1,2-dibromobutane because furanidine is decomposed when passed over alumina, the principal decomposition product being propylene [4].

Literature data: d_4^{20} 1.8204; [14]; n_D^{20} 1.5171 [15]; b.p. 166.3° [16].

The residue left after the 1,2-dibromobutane had been driven off yielded 1,2,3,4-tetrabromobutane, with a m.p. of 116.5-117°.

Thus, reacting furanidine with butylaniline yields N-phenylpyrrolidine, aniline, butene-1, and a small amount of divinyl.

7. Reaction of furanidine with an aniline-cyclohexylamine mixture. a) A reaction mixture consisting of 18 g of furanidine, 11.5 g of aniline, and 12.4 g of cyclohexylamine* (molar proportions 2:1:1) was passed over alumina at 400°. The customary processing of the catalyzate yielded the following reaction products: 6.3 g of cyclohexene (60.5% of the theoretical):

B.p. 81-82° (754 mm); n_D^{20} 1.4460; d_4^{20} 0.8105; MR_D 27.03; computed for C_6H_{10} 27.24.

Literature data: b.p. 84° (763 mm); d_4^{20} 0.8112; n_D^{20} 1.4469 [18].

6.8 g of aniline (60% of the quantity placed in the reaction) with a b.p. of 69.71° at 9 mm, n_D^{20} 1.5790; acetanilide m.p. 112.5°; and 0.7 g of N-phenylpyrrolidine (4% of the theoretical, based on the furanidine placed in the reaction, and 9.5% of the theoretical, based on the reacted aniline):

B.p. 110-112° (8 mm); n_D^{20} 1.5871; d_4^{20} 1.0253; MR_D 48.26; computed for $C_{10}H_{13}NF_3$ 46.51; EM_D 1.75.

5.210 mg substance: 0.4111 ml N_2 (22°, 760 mm). 5.600 mg substance: 0.4460 ml N_2 (20°, 760 mm). Found %: N 9.13, 9.26. $C_{10}H_{13}N$. Computed %: N 9.52.

An attempt to isolate N-cyclohexylpyrrolidine from the aniline fraction by treating the latter with p-toluene sulfochloride met with failure.

b) A reaction mixture of 9 g of furanidine, 11.5 g of aniline, and 12.4 g of cyclohexylamine (molar proportions 1:1:1) was passed over alumina in a current of nitrogen at 400°. The following reaction products were recovered: 6.7 g of cyclohexene (67% of the theoretical):

B.p. 81-83° (762 mm); n_D^{20} 1.4411; d_4^{20} 0.8085; MR_D 26.84; computed for C_6H_{10} 27.24.

7.2 g of aniline (62.5% of the quantity placed in the reaction), b.p. 67-69° (9 mm), n_D^{20} 1.5781; acetanilide m.p. 113°; and 1 g of N-phenylpyrrolidine (60% of the theoretical, based on the furanidine placed in the reaction, and 14.5%, based on the reacted aniline):

B.p. 120-122° (12 mm); n_D^{20} 1.5844; d_4^{20} 1.0182; MR_D 48.48; computed for $C_{10}H_{13}NF_3$ 46.51; EM_D 1.92.

Thus, reacting furanidine with a cyclohexylamine-aniline mixture yields cyclohexene and N-phenylpyrrolidine, no N-cyclohexylpyrrolidine being formed, no matter whether the molar proportions are 2:1:1 or 1:1:1.

8. Reaction of furanidine with cyclohexylaniline. A mixture of 9 g of furanidine and 21.6 g of cyclohexylaniline** (molar ratio 1:1) was passed over alumina at 400°. The customary processing of the catalyzate yielded the following reaction products: 6 g of cyclohexene (60% of the theoretical):

B.p. 79-80° (754 mm); n_D^{20} 1.4425; d_4^{20} 0.8064; MR_D 27.00; computed for C_6H_{10} 27.24.

*The cyclohexylamine was synthesized from cyclohexanone, formic acid, and ammonium carbonate [17].

**The cyclohexylaniline was synthesized from cyclohexanone and formanilide [17].

6.7 g of aniline (59% of the theoretical), n_D^{20} 1.5789; acetanilide m.p. 112.5-113°; and 1 g of N-phenylpyrrolidine (6% of the theoretical, based on the furanidine placed in the reaction, and 13.5%, based on the reacted cyclohexylaniline):

B.p. 87° (3 mm); n_D^{20} 1.5840; d_4^{20} 1.0257; MR_D 48.05; computed for $C_{10}H_{13}NF_3$ 46.51; EM_D 1.54.

Thus, reacting furanidine with cyclohexylaniline yields cyclohexene and N-phenylpyrrolidine, no N-cyclohexylpyrrolidine being formed at all.

SUMMARY

The results of our study of the comparative activity of aniline and aliphatic amines in the reaction with furanidine, as well as in the reaction of furanidine with secondary aliphatic-aromatic amines, leads to the following conclusions:

1. The reactinn of furanidine with ethylamine – aniline, propylamine – aniline, butylamine – aniline, and cyclohexylamine – aniline mixtures yields N-phenylpyrrolidine.

2. The reaction of furanidine with the secondary aliphatic-aromatic amines: ethylaniline, propylaniline, butylaniline, and cyclohexylaniline, yields N-phenylpyrrolidine, unsaturated hydrocarbons (alkenes), and negligible amounts of divinyl.

LITERATURE CITED

[1] Yu.K.Yuryev, I.K.Korobitsyna, and M.Ya.Kuznetsova, J.Gen.Chem. 20, 1493 (1950).

[2] N.Hall, M.Sprinkle, J.Am.Chem.Soc., 54, 3469 (1932).

[3] C.Smyth, W. Walls, J.Am.Chem.Soc., 54, 3230 (1932).

[4] Yu.K.Yuryev, "The Conversion of Heterocyclic Compounds Containing Oxygen into Ring Systems Containing Other Heterocyclic Atoms and into Hydrocarbons" Sci. Rep. Moscow State Univ. 79, 118, 148, 154, 121 (1945); J.Gen.Chem. 9, 153 (1939); Ibid, 7, 2945 (1937).

[5] Yu.K.Yuryev and F.F.Shenyan, J.Gen.Chem. 4, 1258 (1934).

[6] R.Anschutz, Ann., 221, 137 (1883).

[7] T.Patterson, D.Thomson, J.Chem.Soc., 93, 37- (1908).

[8] M.D.Tilicheev, J.Russ.Chem.Soc. 57, 149 (1925).

[9] G.Ciamician, P.Magnaghi, Ber., 19, 570 (1886).

[10] R.Jacobson, J.Am.Chem.Soc., 54, 1545 (1932).

[11] A.Zander, Ann., 214, 175 (1882).

[12] W.Kahlbaum, J. Phys.Chem., 26, 626 (1898).

[13] B.K.Merezhkovsky, Ann., 431, 118 (1923).

[14] N.Grabovsky and A.Zaitsev, Ann., 179, 332 (1875).

[15] H.Lucas, R.Dillon, J.Am.Chem.Soc. 50, 1463 (1928).

[16] J.Timmermans, Bull. Soc. Chim. Belg., 36, 504 (1927).

[17] Yu.K.Yuryev and I.K.Korobitsyna, Bull. Moscow State Univ., 1950, No. 3, 87.

[18] S.S.Nametkin, J.Russ.Chem.Soc. 55, 59 (1924).

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